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The Relationship Between Atmospheric Deposition and the Concentration of 19 PCB Congeners in 5 Inland Lakes in Ontario

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ABSTRACT

This study was conducted to determine the relationship between atmospheric deposition and the concentration of 19 PCB congeners in five inland lakes in Ontario, Canada. Four of these lakes (Wood Lake, Boshkung Lake, St. Nora Lake, Opeongo Lake) are relatively isolated and one of the lakes (Lake Scugog) is substantially developed, but none of the lakes has any direct sources of PCBs. Samples of several groups of biota, sediments, water and suspended solids were collected from the lakes in the fall of 1986 and the spring of 1987. It was concluded that atmospheric deposition resulted in total congener concentrations of 1-2 ng L^{-1} dissolved in water, 10 - 50 ng g^{-1} in sediment, approximately 10 ng g^{-1} in biota from lower trophic levels, and approximately 30 ng g^{-1} in biota from upper trophic levels. Although the congener distribution changed subtly between lakes and species, the trichlorobiphenyl, 31(28) was the most prevalent congener in four of the study lakes, followed by the hexachlorobiphenyls, 153 and 138. This pattern correlated well with the congener distribution reported in the literature for the atmospheric vapour phase and precipitation. The fifth lake (Boshkung Lake) contained a larger number of congeners and it was concluded that the source of PCBs to the lake was different than to the other lakes. No lake had consistently higher concentrations of total PCBs (wet weight) in biota. On a lipid basis, there was no difference in total PCB concentration between lakes for all groups of biota. Within the lakes, yellow perch had significantly higher concentrations of total PCB than most other groups, except for smallmouth bass. In two of the lakes the congener pattern was consistent through all trophic levels, while in the rest of the lakes there was a significant shift to the higher chlorinated congeners in the upper trophic levels. The higher total PCB concentrations, and the selective accumulation

of higher chlorinated congeners, in the yellow perch and smallmouth bass were attributed to species-specific factors such as growth and metabolic rates, in addition to lake-specific effects, such as differences in productivity.

INTRODUCTION

The movement of anthropogenically derived compounds through the atmosphere, with subsequent deposition by wet and dry processes, is the major transport mechanism to isolated areas. The effects of this transport are well documented in the case of acidic deposition but the extent and significance of the problem with regard to organochlorine contaminants in general, or polychlorinated biphenyls (PCBs) specifically, is still unclear. Strachan and Eisenreich (1988) estimated that deposition of PCBs from the atmosphere was responsible for approximately 90% of the total PCBs entering Lake Superior, 78% in Lake Huron and 58% in Lake Michigan. Similarly, Johnson et al. (1987) estimated that direct precipitation accounted for greater than 90% of the organochlorine loadings, including PCBs, to 5 lakes in two watersheds in Ontario, Canada. Evidence from peat bog cores collected in the northern U.S. and central and eastern Canada has shown that the current atmospheric loadings rates are approximately 1.3 to 3.0 ug m^{-2} y^{-1} (Rapaport and Eisenreich 1988), values which closely correlate with levels determined from net sedimentation rates in isolated lakes (Swackhamer and Armstrong 1986). The peat bog data also suggest that current atmospheric loading rates are considerably lower now than in the past (Rapaport and Eisenreich 1988).

Although atmospheric loading levels are low, and are probably declining as a result of restrictions on the use of PCBs imposed in the mid-1970's, several studies indicate that the rates of input are high enough to permit accumulation of the PCBs to levels that approach the IJC guidelines for the protection of piscivorous birds. In Ontario, Johnston et al. (1987) reported maximum mean concentrations (wet weight basis) of 53.9 ug kg^{-1} in northern pike (Esox lucius) on the Bruce Peninsula and 66.3 ug kg^{-1} (wet weight) in brook trout (Salvelinus fontinalis) in the Turkey Lake region. Several organochlorine contaminants have been reported in the biota of Siskiwit Lake, an isolated Lake on Isle Royale in Lake Superior, and PCBs in the lake trout (Salvelinus namaycush) have reached concentrations of 34 μg g^{-1} on a lipid

weight basis (Swackhamer and Hites 1988).

We are aware of no studies that have related the congner composition of PCBs entering the lake through the atmosphere to the subsequent distribution of the congeners in the biotic and abiotic segments of the lake. Although previous studies of Ontario inland lakes (Johnston et al. 1988) and Lake Siskiwit (Swackhamer and Hites 1988) report relatively high concentrations of PCBs in upper trophic levels, the distribution of PCBs throughout the entire lake ecosystem was not reported. Studies of congener distribution in lakes with known point sources of PCBs have shown that the pattern of congeners can remain relatively constant through several trophic levels (Oliver and Niimi 1988), or the pattern can become enriched in more highly chlorinated congeners in the upper trophic levels (van der Oost et al. 1989).

The goal of the present study is to ascertain the concentration of 19 PCB congeners in representative groups of biota and abiotic compartments in a number of inland lakes to determine: 1) the concentration of PCBs which can be attributed to atmospheric deposition; 2) the consistency of the congener distribution among the lakes; 3) the changes in distribution of the congeners through the biotic community and the abiotic compartments of sediments, water and suspended particulate matter. It is our hypothesis that all of the inland lakes will show a consistent pattern of PCB congeners which can be directly related to atmospheric input, but there are also subtle, lake-specific variations in the distribution of congeners between biotic and abiotic compartments.

MATERIALS AND METHODS

Study Area

Five lakes were chosen for the present study. Initial selection of the lakes was based on monitoring data from the Ontario Ministry of the Environment's Sport Fish Testing and Information Program, which reported total PCB concentrations for lake trout and smallmouth bass muscle to be below or near 20 ng g^{-1}. Final selection of the lakes was based on the presence of golden shiner (Notemigonus crysoleucas Mitchill), bluntnose minnow (Pimephales notatus Rafinesque), yellow perch (Perca flavescens Mitchill), smallmouth bass (Micropterus dolomieui Lacépède) and, where possible, lake trout (Salvelinus namaycush

Walbaum). These species represented several trophic levels and habitats within the lakes.

The five study lakes are located in central Ontario, Canada (Fig 1). The lakes are situated in several different townships and counties (Table 1), in areas which range from agricultural land (Lake Scugog), to cottage property (Boshkung Lake, St. Nora Lake, Wood Lake), to a provincial park (Opeongo Lake). In addition, the lakes are situated from 20 km (Scugog) to 200 km (Opeongo) northeast of the major industrial centers near western Lake Ontario ("The Golden Horseshoe").

Sampling

All sampling of biota, water and sediments was conducted in August to November 1986 and May to July 1987. Adult yellow perch, smallmouth bass and lake trout were caught with a 1.3 or 2.6 m trap net. Some older and young-of-the-year yellow perch, golden shiner and bluntnose minnow were collected using a 20 m bag seine. Crayfish (Cambarus sp.), clams (Elliptio complanata) and miscellaneous invertebrates (primarily trichopteran, ephemeropteran and odonate insect larvae) were collected using hand-held dip nets. Zooplankton were collected using a 0.25 m^2 conical net made of canvas, 276 μm nytex mesh and a brass cod bucket. Tows were made for approximately 5 minutes at a depth of 5 - 10 m, and the plankton collected in 2-3 tows grouped to give one sample. The plankton were further concentrated by passing the sample through 64 μm mesh. With the exception of the trap nets, all sampling equipment were soaked in reagent grade methanol prior to use.

Generally, samples of biota were collected in several areas of the lake to give a representative sample of that particular species for that lake. This was usually the case with pelagic species such as lake trout and smallmouth bass where the fish were distributed throughout the lake, however, in some species of fish (golden shiner) and invertebrates (clams, crayfish), samples were only available in areas where sediment conditions were appropriate. Whenever possible, samples were collected from more than one location, and the data combined.

Total body weight and length of all fish were measured in the field before dissection and freezing. Samples were stored as whole fish in acetone-hexane rinsed aluminum foil. Muscle samples used for PCB analysis were removed from the fish carcass just before the extraction procedure. Samples of muscle tissue

were taken from the dorsal area of the fillet below the dorsal fin for lake trout, smallmouth bass and adult yellow perch samples. With smaller fish (golden shiner and bluntnose minnow), the head, tail and internal organs were removed before analysis. Crayfish samples consisted of muscle dissected from the tail, and clam samples consisted of soft tissue removed from the valves.

Sediment cores were collected from the deepest area of each lake (Fig 1) using a K-B corer with brass tubes 0.35 m in length. After collection of the core, a plug was inserted into the bottom of the tube and the core elevated by 3 cm. The upper 3 cm of each core were removed with an acetone-hexane washed aluminum sectioning device, and stored in solvent washed 250 ml Mason jars. Sediments samples to be analysed for total organic carbon were collected in the same area as those for residue analysis, using an Ekman grab sampler.

Water and suspended solids samples were collected by hand pumping water with a solvent rinsed, stainless steel and teflon pump from a depth of approximately 1 m into a stainless steel container. Volumes of 18 L of lake water were passed through 137 mm diameter organic binder-free filters (pore size of 0.3 μm) into a 20 L stainless steel extraction vessel. Two volumes (500 and 400 ml) of distilled-in-glass methylene chloride were added to the water in the extraction vessel, each stirred for 15-20 min, and removed into a 1 L amber glass bottle by displacement with nitrogen gas. Suspended solids which were retained on the 0.3μm filters were stored solvent washed 250 ml Mason jars with approximately 100 ml of methylene chloride. Grab samples of water were also collected for pH, alkalinity, suspended solids and dissolved organic carbon (DOC).

All sediment, suspended sediment and biota samples were stored temporarily in 250 ml or 500 ml Mason jars which had been rinsed with reagent acetone and pesticide grade hexane and sealed with solvent rinsed aluminum foil. All biota samples were frozen within 8 h of collection and remained frozen until analysis.

Sample Preparation

Sediment samples of approximately 5 g were prepared for analysis according to method "A" of the Ontario Ministry of the Environment protocol for analysis of organochlorine pesticides and PCBs in sediments (OME, 1983). Briefly, sediments were sonified with acetone, and back-extracted into methylene

chloride. The extract was dried by passing through sodium sulphate and rotary evaporated to 2 ml for sample cleanup and fractionation. Samples were cleaned up and fractionated into three subfractions by column chromatography (1 cm i.d.) on 5 g of activated silica gel (60-200 mesh). The column was eluted with 40 ml of hexane to yield Fraction A (PCBs, DDE, aldrin, lindane, heptachlor, and mirex). The column was subsequently eluted with 40 ml of 25% methylene chloride in hexane, and 40% methylene chloride in hexane to yield organochlorine pesticide subfractions B and C, respectively. Sulfur compounds were removed from Fraction A by precipitation with mercury.

Biota samples of approximately 5 g were ground with sodium sulphate in a mortar, and extracted into hexane on a Soxhlet apparatus for 1 h. A subsample of the extract was rotary evaporated to 2 ml and made up to 5 ml in 55:45 hexane:methylene chloride. Lipids were removed from this extract by gel permeation chromatography on a 3 cm i.d. X 28 cm column of Biobeads SX2 (200-400 mesh). The column was eluted at a rate of 2 ml per minute with 55:45 hexane:methylene chloride. The first 90 ml of eluent, which contained lipid, was collected and evaporated to dryness for gravimetric determination of lipid content. The next 100 ml of eluent, which contained PCBs and organochlorine pesticides, were collected and subjected to further cleanup before analysis. The extract was cleaned up and fractionated by silica gel column chromatography, as described for the sediment extracts.

The methylene chloride collected in the field from two water samples (2 x 18 L) was pooled and passed through sodium sulphate and rotary evaporated to 2 ml. The extract was partitioned into hexane by successive additions of hexane and evaporation under nitrogen. The sample was then cleaned up and fractionated by silica gel chromatography, as described above. The glass fibre filters containing suspended particulate material were manually broken up while immersed in the methylene chloride originally added in the field. The entire sample was filtered under suction through sodium sulphate in a Buchner funnel. A further 150 ml of methylene chloride was then passed through the filter. The extracts from two 18 L samples of suspended sediments were pooled. The pooled extract was partitioned into hexane and cleaned up/fractionated by silica gel chromatography, as described previously.

Sample Analysis

Sediment samples were analysed for organic carbon content, and the water samples were analysed for pH, alkalinity, suspended solids and DOC according to Ontario Ministry of the Environment protocols (OME 1983).

Samples were analyzed for PCBs by high resolution gas chromatography on a Varian 3500 gas chromatograph with ECD, using a 30 m DB5 capillary column (250 μm OD, 25 μm ID) and splitless injection. The flow of hydrogen carrier gas was 1.8 ml/min and the flow of nitrogen make-up gas into the detector was 28 ml/min. GC conditions were: injector 250°C, detector 275°C, and initial column temperature 80°C. The column temperature was programmed as follows: 1 minute hold time at 80°C, increase at 4°/min to 160°C, increase at 1.5°/min to 230°C, increase at 7°/min to a final temperature of 250°C, with a final hold time of 20 min. Individual congeners were identified by retention time (window 0.02 %), and quantified from integrated peak areas.

Quantification of individual PCB congeners was by comparison to standards purchased from the National Research Council in Halifax, Canada. The standard was a mixture of the NRC standards CLB-1 A and D, to which congener 52 (2,2',5,5') was added. DDE was added as a relative retention time marker. Rather than quantify all PCB congeners, 19 major congeners were selected for analysis (Table 2). These particular congeners were chosen because: a) they represented a wide range of chlorination, from trichlorobiphenyls to decachlorobiphenyl; b) they included several of the major congeners in commercial Aroclors (Shulz et al., 1988) and in environmental samples (Oliver and Niimi, 1988; Norstrom et al., 1988; Baker and Eisenreich, in press); c) they were generally free of coeluting peaks on a DB-5 capillary column; d) standards of the individual compounds were available.

Of the 19 congeners quantified from the standard, 4 of the congeners coeluted with other PCB congeners present in environmental samples (Table 2). All coeluting peaks were reported as the concentration of the congener present in the standard, with the exception of congener 77 (coeluting with congener 110). Since congener 77 (3,3',4,4') makes up a very small proportion of PCBs in commercial Aroclors in comparison to congener 110 (2,3,6,3',4'), it was assumed that no congener 77 was present in the samples of the study lakes. Since there were no purified standards of congener 110 available, congener 77 in the standard was used as a retention time marker for 110 and was

used to calculate concentrations of 110 in Lake Clear samples. The integrated area of the peak eluting at the retention time for 77 was multiplied by the response factor for congener 77 times the ratio of the relative response factors for congeners 77 and 110, as determined by Mullin et al. (1984).

Extraction efficiencies for all quantified PCB congeners were determined by analyses of spiked samples to be >85% for biota and sediment samples, and >75% for water and suspended sediment solids samples. Data are reported without correction for extraction efficiencies. Sample blanks were run at intervals of approximately every 8 samples. Analysis of replicates of muscle tissue (n=5) removed from each of 3 perch and 3 smallmouth bass, and analysis of replicates (n=3) from 3 sediment samples indicated that between-replicate variability was less than 10%.

Analytical detection limits for individual congeners, which are listed in Table 3, were determined by two methods. It was determined that peaks with integrated areas of >1000 could be detected over background noise. Using a threshold area of 1000 and the detector response factors, the detection limits of the various congeners could be calculated in ng ml^{-1}. The chromatography data system was set to ignore all peaks with areas <1000. In addition, these theoretical detection limits were tested and adjusted, if necessary, by analyzing serial dilutions of the PCB standard and selected sample extracts. The EC detector responded linearily over the range of PCB concentrations in sample extracts. Peak identification, congener concentrations, and the efficiency of the silica gel fractionation procedure were confirmed by GC/MSD analysis of selected samples.

Data Treatment and Statistical Analysis

The concentration of each congener in biota samples was calculated on a wet and lipid weight basis, while concentrations in sediment samples were calculated on the basis of dry weight and organic carbon weight. In this report, "total PCB" is defined as the sum of the 19 congeners. The congeners represent 46%, 53%, and 62% of the total PCBs present in Aroclors 1242, 1254, and 1260, respectively (Murphy et al. 1987). Comparisons between packed and capillary column analysis of sediment samples (Ferguson and Metcalfe, in press) indicated that the sum of the 19 congeners represented approximately 70% of the the total PCBs detected by low resolution GC. The proportion of each congener

is calculated as the concentration of the congener divided by the total. This latter value gives the relative contribution of a particular congener to the total PCB concentration.

Data were analysed using SPSS/PC Ver 2.0 statistical software (SPSS/PC, Inc., Chicago, Ill. 1988) on a personal computer. All means and range tests were calculated using log transformed data to equalize variances and normalize residuals. Significant differences were measured at the 0.05 level (i.e. $P<0.05$). Zero values (i.e. below detection limits) were replaced by random numbers for discriminate analysis of the proportionate data (Sharaf et al., 1986).

RESULTS

Morphometric and water chemistry data for the five study lakes are presented in Table 4. Four of the lakes (Boshkung, Wood, St. Nora and Opeongo) are similar with respect to the water chemistry and morphometry, and can be classified as deep, oligotrophic lakes. The organic carbon content of sediments from these four lakes ranges from 3.6% in Boshkung to 9.9% in Opeongo. In contrast, the water chemistry and morphometry data for Lake Scugog indicates that this lake is a shallow, relatively eutrophic lake.

Congener concentrations in water were often near detection limits, but total PCBs in water ranged from a low of 0.83 ng L^{-1} in Lake Scugog to 1.85 ng L^{-1} in Wood Lake. Data for PCBs associated with suspended solids are available for only three lakes. The lowest total PCB concentrations in suspended solids were observed in Lake Scugog and the highest in Wood Lake. In sediment, total PCB concentrations ranged from 12 to 54 ng g^{-1} on a dry weight basis and 0.13-0.55 $\mu g\ g^{-1}$ on an organic carbon basis.

Total PCB concentrations in biota on a wet weight basis ranged from 2.7 ng g^{-1} (zooplankton in Lake Scugog) to a maximum of almost 70 ng g^{-1} in lake trout in Boshkung Lake (Table 5). Comparisons between PCB concentrations on a lipid weight basis for the same biota in different lakes showed that there was little interlake variability. Indeed, all biota from all of the lakes showed very similar total PCB concentrations on a lipid weight basis (1 to 4 $\mu g\ g^{-1}$).

Comparisons of body weight, lipid content, and total PCB concentrations in biota using one-way analysis of variance showed

few consistent trends. With the exception of the clam samples, there were no significant differences in body weight between lakes for any of the biota. This is consistent with the age data which showed that mean age of yellow perch from all lakes was approximately 3 years and all smallmouth bass were approximately 4+ years old. Lipid levels in yellow perch, smallmouth bass, bluntnose minnow and clams were not significantly different between the lakes, but lipid levels were higher in golden shiner and zooplankton from Opeongo Lake in comparison to other lakes.

No one lake showed consistently higher concentrations of total PCBs in all classes of samples. However, Boshkung Lake and Opeongo Lake were significantly higher than other lakes in two or more classes of samples. For example, on a wet weight basis, PCB levels in zooplankton and smallmouth bass in Boshkung Lake were significantly higher than in Opeongo, Wood and Scugog. Similarly, the clam samples from Boshkung Lake contained levels of PCBs significantly higher than in St. Nora or Wood Lake. Both the golden shiner and sediment (dry weight) samples from Lake Opeongo were significantly higher than any of the other study lakes. On a lipid basis, there were no significant differences in PCB concentration between any of the lakes for all biota, with the single exception of golden shiners from Wood Lake, which contained more PCBs than shiners from Opeongo Lake.

Comparisons between total PCB levels on a wet weight basis among the various groups of biota (e.g. most contaminated biota group vs least contaminated biota group) indicated that there was no consistent pattern across all of the lakes. For example, smallmouth bass contained among the highest PCB levels of all biota in Boshkung Lake but contained among the lowest levels in both Lake Scugog and Opeongo Lake.

These patterns were somewhat simpler when comparing total PCB on a lipid weight basis. In all lakes, adult yellow perch contained significantly higher concentrations of total PCB than at least one other group of biota. The only exception was Lake Scugog, where yellow perch had the highest mean concentration but differences between other groups of biota were not statistically significant. Levels of PCBs in perch samples were significantly greater than levels in zooplankton and golden shiner in Boshkung Lake, bluntnose minnow in Wood Lake, miscellaneous invertebrates and golden shiner in St. Nora Lake, and golden shiner, bluntnose minnow and zooplankton in Opeongo Lake. Total PCB concentrations on a lipid weight basis in lake trout samples were not as high as in yellow perch samples.

These relationships were also tested using 2-way ANOVA on the log-transformed total PCB data (lipid weight basis) for 6 species common to Boshkung, Wood, St. Nora and Opeongo (zooplankton, clam, golden shiner, bluntnose minnow, yellow perch, smallmouth bass). Lake Scugog was excluded from this analysis because no samples of golden shiner or clams samples were available. The analysis again indicated that the difference between lakes was not significant ($p>0.05$), while the differences between species was highly significant ($p<0.001$). As a result, the data were pooled (Table 6) and range tests conducted to determine significant differences between the species. The PCB data for lake trout collected from three lakes are included in Table 4 for comparison, but these data were not included in the ANOVA or range tests.

The range tests on the PCB concentration (lipid weight) data showed that the highest PCB levels were observed in the yellow perch samples (Table 6), which were significantly higher than all other groups except smallmouth bass. Both smallmouth bass and clams contained significantly higher concentrations of PCBs than golden shiner and bluntnose minnow.

The relative proportion of individual PCB congeners in five groups of biota and sediments are presented in Figure 2 for four of the study lakes. Congener proportion data for water and suspended solid samples were not included because of the high between-sample variability (>25%). The dominant congeners in the individual lakes include the trichlorobiphenyl combination of 31(28) and the pentachlorobiphenyl congeners, 153 and 138. Congener data for Lake Scugog, which are described by Macdonald and Metcalfe (1990), are not shown because the pattern is similar to St. Nora Lake. The simplest patterns are observed in Opeongo and Wood lakes, where the three major congeners account for approximately 50% of the total PCBs within biota, and all groups of biota have approximately the same pattern. However, sediments in Lake Opeongo show a more uniform range of congeners, including a relatively high proportion of the trichlorobiphenyl congeners 18 and 52, and the pentachlorobiphenyl congener 101.

The distribution of congeners is more variable in St. Nora Lake and Boshkung Lake. With the exception of golden shiners, in which congeners 31(28) account for 56% of the total PCB, the proportion of the individual congeners is more widely distributed in all groups in Boshkung Lake. PCBs in clam, zooplankton and yellow perch samples are comprised primarily of the trichlorobiphenyls, 31(28) and the tetrachlorobiphenyl, 52 with

significant amounts of congener 110. Smallmouth bass and sediments contain primarily penta- and hexachlorobiphenyls, 110, 118, 153 and 138. This same general pattern is observed in St. Nora Lake samples, although the trichlorobiphenyls comprise a much larger proportion of the total PCBs. In both Boshkung and St. Nora Lakes, there is a shift in the upper trophic levels to the more highly chlorinated penta- and hexachlorobiphenyls. This shift in congener distribution with trophic levels is also present among biota in Lake Scugog (Macdonald and Metcalfe 1990). In contrast, no significant change in congener pattern was seen in biota from Wood Lake, Opeongo Lake (Figure 2).

Discriminant analysis of the congener proportion data shows that the patterns of congener distribution are not markedly different in the study lakes (Figure 3). However, the lake of origin can be properly identified for a relatively high proportion of the samples (approximately 70%). Congener 209 was removed from analysis because of the large number of values below the detection limit. The first discriminant function accounted for 71% of the total variance, and separated Boshkung Lake and St. Nora Lake on the basis of congeners 110, 196, 118 and 87 (in descending order of correlation), and Opeongo Lake and Wood Lake on the basis of congeners 138 and 153. The second function accounted for only 16.5% of the total variance and separated Boshkung and Wood on the basis of the proportion of the trichlorobiphenyl 31(28), and St. Nora Lake and Opeongo Lake by the proportion of congeners 49, 151 and 195. With the three discriminant functions, Opeongo Lake was successfully classified at 96.3% of the time, followed by Boshkung Lake (73.1%), St. Nora Lake (60.0%) and Wood Lake (59.3%). For the four lakes, 72.4% of the samples were properly classified with the three discriminant functions.

Discriminant analysis indicates that the congener distribution in sediment and biota samples from the study lakes is markedly different from the congener distributions in two other lakes (Lake Clear, Rice Lake) which have received historical inputs of commercial PCB Aroclors (Macdonald and Metcalfe 1990). As illustrated in Figure 4 using Opeongo Lake and Wood Lake as examples of lakes receiving atmospheric PCBs, the congener distributions are widely separated by discriminant function analysis from a lake contaminated with Aroclor 1254 (Lake Clear) and a lake contaminated with Aroclors 1242, 1254, and 1260 (Rice Lake). The first discriminant function (78% of total variability) separates the two pristine lakes from the

others, primarily by the high proportion of 31(28). The second function (15% of total variability) separates out Rice Lake on the basis of a higher proportion of congeners 138, 153, 180 and 170 in the other 3 lakes. In total, over 95% of the samples were properly classified as coming from Lake Clear, Rice Lake, or from a pristine lake with the two discriminant functions. Similarily, Macdonald and Metcalfe (1990) showed that Lake Scugog samples are easily distinguished from Lake Clear and Rice Lake samples by the same discriminant function analysis.

Within the lakes receiving atmospheric PCBs, classification of samples by group indicated that the congener pattern could classify the patterns to the appropriate group 70% of the time on the basis of three significant discriminant functions which accounted for 48.5%, 25% and 11% of the variability, respectively. The first function separated sediment from the other samples on the basis of congeners 52, 201 and 118 (in descending order of correlation), and golden shiner and zooplankton on the basis of the higher proportions of congeners 31(28). The second function grouped smallmouth bass and yellow perch together on the basis of higher proportions of congeners 180, 201 and 44.

DISCUSSION

The goal of this study was to ascertain the role of atmospheric deposition in determining the concentration of PCBs in the biota and sediments in inland lakes in Ontario, Canada. However, since precipitation measurements were not conducted during this study, the pattern and amount of PCBs entering the study lakes must be estimated from data reported in the literature. Since approximately 90% of the PCB loadings to isolated lakes in Ontario are deposited directly from the atmosphere (Johnston et al. 1988), it is to be expected that the dominant congener pattern in these lake should resemble the distribution in the atmosphere, with predictable differences due to losses from volatilization and sedimentation (Swackhamer et al. 1988).

It has been established that PCBs exist predominantly in the vapour phase in the atmosphere (Atlas et al. 1986; Duinker and Bouchertall, 1989), but it has been suggested that the flux of PCB occurs primarily by wet and dry deposition of PCBs associated with particulates (Swackhamer et al. 1988). Partitioning of

individual congeners within the atmosphere results in an enrichment of higher chlorinated congeners on the particulate fraction and lower chlorinated congeners in the vapour phase (Swackhamer et al. 1988; Duinker and Bouchertall 1989). Analysis of rain, particulate and vapour samples in 4 urban air samples collected in Europe has shown that the particulates and rain are dominated by the hexachlorobiphenyls 153 and 138, with a significant amount of the tetrachlorobiphenyl 52 and hexachlorobiphenyl 101 (Duinker and Bouchertall 1989). Vapour phase samples are dominated, however, by trichlorobiphenyls (Duinker and Bouchertall, 1989; Baker and Eisenreich, in press). Predominance of the higher chlorinated congeners in precipitation has been shown in peat bog cores (Rapaport and Eisenreich 1988), directly in precipitation (Murphy and Rzeczutko 1977) and in air samples (Eisenreich et al. 1981).

Although substantial shifts in congener composition within the biota of some lakes make characterization of patterns for the lakes difficult, four of the five study lakes (excluding Boshkung Lake) show congener patterns which compare well with the patterns reported for precipitation and the atmospheric vapour phase (Murphy and Rzeczutko 1977; Rapaport and Eisenreich 1988; Swackhamer et al. 1988; Duinker and Bouchertall 1989). All samples of biota collected in Opeongo Lake and Wood Lake show high proportions of congeners 153 and 138 (Fig. 2). This also compares well with the PCB congener pattern observed in biota in the Canadian Arctic; a region which is exposed to atmospheric input only (Norstrom et al. 1988). However, biota and sediments in all study lakes also contain the trichlorobiphenyl congeners 31(28), which account for approximately 25% of the total PCB pattern in the biota. Together, congeners 153, 138, and 31(28) account for 50-60% of the PCBs in the biota of the two study lakes.

Swackhamer et al. (1988) noted high concentrations of trichlorobiphenyls in rain samples at Siskiwit Lake, and attributed this to scavenging of the more water-soluble congeners from the vapour phase. Subsequently, the trichlorobiphenyls deposited in inland lakes may appear at high concentrations in aquatic biota because they are relatively water soluble, and therefore biologically available for uptake.

Swackhamer et al. (1988) suggested that an increasing proportion of PCBs bound to atmospheric particulates may be lost from the atmosphere as the distance increases between the source and the site of deposition. If we assume that the "Golden

Horseshoe" area of Lake Ontario is the source of particle-bound PCBs to our study lakes, we might expect a lower proportion of congeners 153 and 138 in Opeongo Lake (200 km from Toronto) than the other study lakes. Since this is clearly not the case, we might speculate that the pattern of atmospheric transport and flux of particulate PCBs in this region is more complex than anticipated.

We can conclude from the simplicity of the congener pattern and the similarity with patterns reported for precipitation that atmospheric deposition is the major source to these study lakes. It should also be noted that samples were collected in both the fall and spring, and there is no indication that there are major differences in congener distribution between the two sampling times. This is significant, since input from snow probably favours deposition of particulate-associated PCBs, and low temperatures may reduce volatilization losses of the lower chlorinated congeners.

The congener configuration in Boshkung Lake is more difficult to interpret in terms of atmospheric deposition. Although the proportion of congener 31(28) is high in golden shiners, all other groups of biota show a wide range of congeners which include tri-, tetra-, penta- and hexachlorobiphenyl congeners, with no particular homolog group dominating. There are two possible explanations for this. First, Boshkung Lake is situated at the confluence of three major watersheds which include several lakes. The lack of a distinct pattern in Lake Boshkung may be due to the large watershed area. It is also possible that there is an additional source of PCBs in the watershed which flows into Boshkung Lake (e.g. contaminated road oil). The significant amounts of tetra- to hexachlorobiphenyls, particularly the pentachlorobiphenyl 110, suggest that a PCB mixture such as Aroclor 1254, may have been released in the watershed, although the amount is relatively low. It is not possible to properly test either of these hypotheses here, but the difference in overall pattern between Lake Boshkung and the other lakes indicates that the source of the PCBs is different in Lake Boshkung. In addition, higher concentrations of total PCBs in some groups of biota, reported in this study and in contaminant monitoring programs of the Ministry of the Environment lend support to the possibility of an higher levels of input to the lake, either from atmospheric or additional sources.

One of the aims of the present study was to determine the

concentration of PCBs in inland lakes which can be directly attributed to atmospheric input. Sediments from isolated lakes in Wisconsin indicate that current net deposition rates from the atmosphere are approximately 1.9 μg PCB m y^{-1} (Swackhamer and Armstrong 1986); roughly equivalent to the rates observed in peat bog cores in two Ontario sites (1.3 and 2.9 μg m^{-2} y^{-1}; Rapaport and Eisenreich 1988). Swackhamer and Armstrong (1986), however, estimated a total input level of 7.5 μg m^{-2} y^{-1} to Siskiwit Lake, with the difference between the total input and the amount bound to sediments (5.6 μg m^{-2} y^{-1}) being attributed to losses to the atmosphere through volatilization. These calculations are based on values reported by Murphy and Rzeszutko (1977), which are high relative to other remote areas (Atlas et al. 1986) and probably overestimate the total loading and losses due to volatilization.

Based on an approximate mean input value of 1.5 μg m^{-2} y^{-1} and the surface areas reported in Table 4, the study lakes would currently receive from atmospheric deposition approximately 2.25, 3.84, 10.8, 87.9 and 124 g y^{-1} in Wood, St. Nora, Boshkung, Opeongo and Scugog, respectively. These loadings result in concentrations of approximately 10 to 50 ng g^{-1} dry weight in sediments, 0.8 to 1.9 ng L^{-1} in water, 5 to 10 ng g^{-1} wet weight in the lower trophic levels and 10 to 30 ng g^{-1} in the upper trophic levels for the 19 congeners analysed here. If it is assumed that these 19 congeners comprise about 50% of the total PCBs present in the samples, then total PCB levels would be up to 20 ng g^{-1} wet weight in the lower trophic levels and up to 60 ng g^{-1} in the upper trophic levels. These values correspond well with the values reported for Ontario lakes and other isolated areas. Johnson et al. (1987) reported total PCB concentrations (wet weight), as determined by low resolution pack column gas chromatography, in four species of upper trophic level fish in two Ontario watersheds to be 35-66 ng g^{-1}. The values in the present study are considerably lower than the concentrations reported for lake trout in Siskiwit Lake, but they correspond with the values reported for whitefish in that lake and in Lake Superior (Swackhamer et al. 1988). Swackhamer and Armstrong (1986) reported total PCB concentrations in surface sediments from 4 remote lakes in Wisconsin to be between 2.6 and 89 ng g^{-1} dry weight. The mean total of 17 PCB congener concentrations in the sediments and water of Siskiwit Lake were reported as 48 ng g^{-1} and 2.3 ng L^{-1}, respectively (Swackhamer et al., 1988). The total PCB levels estimated in the present study agree closely with these values, and probably represent the concentration of

background contamination of PCBs in aquatic biota in southern and central Ontario.

These rough estimates of atmospheric input suggest that the total loading of PCBs varies considerably between the study lakes. However, comparison of PCB concentrations within the biota, particularly on a lipid basis, indicate that there are no consistent differences between the lakes for any group. This suggests that the concentration of PCBs to which each group is exposed is the same in each lake. Deposition of PCBs from the atmosphere appears to involve a cyclic mechanism where PCBs enter the surface waters during a precipitation event, followed by volatilization of some congeners back to the atmosphere (Murphy 1984). After entering the lake, the major processes which remove PCBs are volatilization and adsorption onto the organic fraction of biogenic or abiotic suspended matter, followed by sedimentation. Swackhamer et al. (1988) estimated that the losses of PCBs through these two processes were approximately equal in Siskiwit Lake. Hence the amount of PCB available to the biota will depend on a series of transport mechanisms in the lake, in addition to the total PCB input.

Lake Scugog does not resemble the other four study lakes in morphometry and trophic status, and it would be expected that the distribution of PCBs in this lake would be different from the other lakes. However, the close similarity between PCB patterns in Lake Scugog and the other lakes (in particular, St. Nora Lake) indicates that high loading rates over a larger surface area may be balanced by higher losses through volatilization or transport to the sediment. Sedimentation of PCBs may be an important process in Opeongo Lake, where the concentration of PCBs in the highly organic sediment is significantly higher than in the other lakes, even though the concentrations in biota are not significantly higher.

The comparisons of total PCB levels within the lakes clearly shows that PCB accumulation is related to species-specific characteristics and not to total PCB loading into the lake. Yellow perch, and to some extent smallmouth bass, contain significantly greater concentrations of total PCBs than the zooplankton or benthic biota, such as clams and bluntnose minnow. Several studies have shown that PCB accumulation in fish involves uptake through the gills and the gut, both of which are influenced by the metabolic rate, growth rate, and size of the fish (Norstrom et al. 1876; Thomann 1981, 1989; Jensen et al. 1982; Thomann and Connolly 1984). However, recent studies have

proposed that, for compounds with octanol-water partition coefficient of 5-8, food chain transfer is the most significant method of exposure to the upper trophic levels (Connolly and Pedersen 1987; Thomann 1989). The diet of perch consists of zooplankton, insects and small fish, while bass feed on insects, small fish and crayfish (Scott and Crossman 1973); none of which have high concentrations of PCBs in the study lakes. Hence the higher PCB concentrations in the upper trophic levels is probably related to lipid content and species-specific metabolic rates, and not high levels in any of the prey species.

The significance of species-specific parameters is also seen in the distribution of individual congeners throughout the trophic levels within each lake. The patterns of congener distribution within the lakes range from being relatively constant in all biota (Opeongo Lake, Wood Lake) to showing a distinct shift from lower chlorinated to highly chlorinated congeners from the lower to upper trophic levels (St. Nora Lake, Lake Scugog, Boshkung Lake). This is illustrated in Figure 5, in which the proportion of individual congeners are graphed for zooplankton and smallmouth bass for each study lake. The pattern for the lower trophic levels (e.g. zooplankton) is relatively constant, showing a group of congeners which probably reflects the patterns in the water fairly accurately (the altered pattern in Lake Boshkung has been discussed previously). The zooplankton probably reach equilibrium with the PCBs in the water phase relatively quickly, and therefore reflect the pattern of PCBs which are entering the lake from the atmosphere. The smallmouth bass from the same lakes, however, shows a similarity with the zooplankton patterns in Lake Opeongo and Wood Lake only. The other lakes show a clear shift toward the moderately chlorinated penta- and hexachlorobiphenyls. Fish in the upper trophic levels (i.e. the smallmouth bass) probably receive a large proportion of PCBs from their diet and little directly from the water (Jensen et al. 1982, others) so that their pattern results from the differential uptake and clearance of the individual congeners throughout the food web.

These two scenarios of trophic transfer of PCBs in the aquatic environment have been observed elsewhere in two separate studies. Oliver and Niimi (1989) reported a relatively constant congener pattern among biota of lower and upper trophic levels in Lake Ontario. Conversely, van der Oost et al. (1989) reported a shift in congener pattern with trophic level, which was attributed to differences in congener pattern among organisms

which are longer-lived (van der Oost et al. 1988).

An explanation for the two scenarios of trophic transfer of PCBs observed in the present study lakes is probably complex. However, the explanation is probably related to lake productivity or the structure of the food web, in addition to the physical behaviour of the individual compounds. Hence the distribution of congeners through the biotic community involves a complex interaction between characteristics of the lake, the organism, and the contaminant.

This has significant implications for our understanding of PCB distribution in the biota of lakes. We have developed an understanding of PCB behaviour through laboratory-based studies or field studies which focus on a single lake and a single species, such as lake trout (Thomann 1989). A comparison of the congener distribution in lake trout in three of our study lakes (Figure 6) shows that the pattern is dominated by penta- and hexachlorobiphenyls. This is most evident in Opeongo Lake. A series of papers on the fish communities in Lake Opeongo (Martin 1966, Kerr and Martin 1970, Martin and Fry 1972) have documented the trophic structure of the lake, as well as the shifts in the populations of the sport fish in the lake since 1936. Smallmouth bass were introduced to the lake in 1928 and feed primarily on crayfish (80%), insects, and yellow perch (Martin and Fry 1972). Cisco or lake herring (Coregonus artedii) were introduced in 1948 and rapidly replaced yellow perch and insects as the dominant food of lake trout. As of the early 1970s, the cisco diet consisted primarily of insects and benthic organisms and it competed with young lake trout for this resource. If it assumed that cisco have the same complement of PCB congeners that are observed in the other organisms in its trophic levels (golden shiner, yellow perch), then lake trout will be exposed to a pattern of PCBs which are dominated by trichlorobiphenyls. Trout apparently absorb all PCB congeners at approximately the same rate (Niimi and Oliver 1983), but must have the ability to excrete and/or metabolize the lower chlorinated congeners. Smallmouth bass in the same lake feed at roughly the same trophic levels but do not lose the lower chlorinated congeners to the same extent as the lake trout (Figure 5), and hence have a congener complement similar to the diet. Basing predictions of PCB behaviour in lake systems on studies using only trout will give a biased view of the ability of the organisms to remove the lower chlorinated congeners from their tissues.

In summary, the congener patterns observed in the isolated

lakes in this study can be directly attributed to atmospheric deposition. Within the lakes, the distribution of congeners varies according to the species involved and the characteristics of the lake. Further research is required on lakes with different degrees of productivity and water chemistry to determine the influence of these parameters on congener distribution.

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Table 1 - Geographical locations of the study lakes in Ontario.

Lake	Township	Lat./Long.
Lake Scugog	Durham Municipality	44°10'/78°50'
Boshkung Lake	Stanhope Twp.[1]	45°04'/78°44'
St. Nora Lake	Stanhope Twp.[1]	45°09'/78°50'
Wood Lake	Oakley Twp.[2]	45°01'/79°05'
Opeongo Lake	Bowen Twp.[3]	45°42'/79°48'

1 Haliburton County
2 Muskoka Municipality
3 Nipissing District (Algonquin Park).

Table 2 - Summary of PCB congener IUPAC numbers, chlorine number and substitution patterns analysed in the study lakes.

Congener Number[1]	Chlorine Number	Chlorine Substitution
18	3	2,2',5
31(28)	3(3)	2,4',5 (2,4,4')
52	4	2,2',5,5'
49	4	2,2',4,5'
44	4	2,2',3,5'
101	5	2,2',4,5,5'
87	5	2,2',3,4,5'
110(77)	5(4)	2,3,3',4',6 (3,3',4,4')
151	6	2,2',3,5,5',6
118(149)	5(6)	2,3'4,4',5 (2,2',3,4',5',6)
153(132)	6(6)	2,2',4,4',5,5' (2,2',3,3',4,6')
138	6	2,2',3,4,4',5'
180	7	2,2',3,4,4',5,5'
170	7	2,2',3,3',4,4',5
201	8	2,2',3,3',4,5,5',6'
196	8	2,2',3,3',4,4',5,6'
195	8	2,2',3,3',4,4',5,6
194	8	2,2',3,3',4,4',5,5'
209	10	2,2',3,3',4,4',5,5',6,6'

1 - IUPAC numbering system for PCB congeners.

Table 3 - Analytical detection limits for individual PCB congeners, expressed as concentration in the sample extract (ng ml^{-1}), as concentration from a 5 g sample of sediment or biota (ng g^{-1}), or as concentration from a 36 L water sample (pg L^{-1}).

	Detection Limits		
PCB Congener	Standard (ng ml^{-1})	Sediment/Biota (ng g^{-1})	Water (pg L^{-1})
18	0.89	0.27	37
31(28)	0.57	0.17	24
52	0.52	0.16	22
49	0.48	0.14	20
44	0.50	0.15	21
101	0.40	0.12	17
87	0.39	0.12	16
110(77)	0.32	0.10	13
151	0.51	0.15	21
118(149)	0.39	0.12	16
153(132)	0.39	0.12	16
138	0.32	0.10	13
180	0.45	0.14	19
170	0.30	0.10	13
201	0.27	0.08	10
196	0.25	0.08	10
195	0.27	0.09	11
194	0.28	0.09	11
209	0.24	0.07	10

Table 4 - Lake morphometry and water/sediment chemistry for the five study lakes.

	Scugog	Boshkung	Wood	St. Nora	Opeongo
Surface area ($m^2 \times 10^{-6}$)	82.6	7.2	1.5	2.56	58.6
Volume ($m^3 \times 10^{-6}$)	112	165	19	42	856
Mean Depth (m)	1.4	23.0	5.0	16.0	14.6
Maximum Depth (m)	7.6	68.0	14.0	39.0	49.4
pH	8.2	7.2	6.9	6.9	7.1
Alkalinity (mg $CaCO_3$ L^{-1})	132	10.4	5.16	4.4	6.9
DOC (mg L^{-1})	8.7	2.9	3.6	2.6	4.0
Susp. solids (mg L^{-1})	24.0	0.9	1.1	1.0	1.0
Sediment OC (%)	16.0	3.6	9.8	5.3	9.9

Table 5 - Geometric mean values of body weights, lipid content and PCB concentrations (lipid and wet weight basis). Values in brackets are the standard deviations about the mean. n.s. = not sampled, because species not present or in low numbers.

	Scugog	Boshkung	Wood	St. Nora	Opeongo
A) ABIOTIC					
water					
sample size	2	2	2	2	2
PCB concentration	0.83	0.93	1.85	1.60	1.23
(ng L^{-1})	(0.49-1.41)	(0.82-1.05)	(0.86-3.99)	(1.51-1.69)	(0.99-1.52)
suspended solids					
sample size	2	-	2	-	2
PCB concentration	47.8	-	367	-	220
(ng g^{-1} d.w.)	(33.7-67.7)	-	(335-402)	-	(176-274)
sediment					
sample size	5	5	4	5	4
organic carbon (%)	16.0	3.6	9.8	5.28	9.87
PCB concentration:					
dry weight	21.2	27.2	15.2	12.0	53.9
basis (ng g^{-1})	(17.9-25.0)	(19.7-37.6)	(14.0-16.5)	(9.47-15.1)	(44.4-65.5)
organic C	0.13	0.36	0.16	0.23	0.55
basis (ug g^{-1})	(0.11-0.16)	(0.26-0.49)	(0.14-0.17)	(0.18-0.29)	(0.45-0.66)
B) BIOTIC					
zooplankton					
sample size	5	2	5	1	4
lipid (%)	0.22	0.62	0.35	0.28	1.42
	(0.17-0.27)	(0.14-2.85)	(0.29-0.42)	-	(0.49-4.12)
PCB (w.w.)	2.73	46.5	3.56	4.36	6.11
	(2.02-3.71)	(41.3-52.3)	(3.00-4.23)	-	(5.18-7.22)
PCB (lip.)	1.27	0.59	1.03	1.55	0.77
	(0.79-2.03)	(0.59-0.60)	(0.74-1.43)	-	(0.66-0.90)
crayfish					
sample size	5	ns	ns	ns	ns
body weight (g)	28.0	ns	ns	ns	ns
	(20.4-38.5)				
lipid (%)	0.26	ns	ns	ns	ns
	(0.13-0.49)				
PCB (w.w.)	8.48	ns	ns	ns	ns
	(2.84-25.3)				
PCB (lip.)	3.32	ns	ns	ns	ns
	(1.04-10.6)				

	Scugog	Boshkung	Wood	St. Nora	Opeongo
clam					
sample size	ns	5	5	5	5
body weight (g)	ns	32.5	8.33	8.74	26.7
	-	(29.5-35.9)	(5.24-13.2)	(6.67-11.4)	(25.1-28.3)
lipid (%)	ns	0.35	0.28	0.14	0.39
	-	(0.26-0.48)	(0.23-0.34)	(0.05-0.44)	(0.34-0.45)
PCB (w.w.)	ns	8.16	4.63	3.57	6.32
	-	(6.09-10.9)	(3.83-5.60)	(2.52-5.06)	(2.10-7.20)
PCB (lip.)	ns	2.33	1.67	1.59	1.62
	-	(1.85-2.9)	(1.40-1.99)	(0.83-3.03)	(1.35-1.95)
golden shiner					
sample size	ns	5	3	4	4
body weight (g)	ns	7.90	6.40	5.58	8.17
	-	(4.55-13.7)	(4.18-9.81)	(4.51-6.91)	(7.95-8.38)
lipid (%)	ns	0.85	0.37	0.76	2.48
	-	(0.70-1.02)	(0.33-0.41)	(0.46-1.26)	(2.25-2.73)
PCB (w.w.)	ns	5.44	4.25	5.20	11.9
	-	(3.88-7.62)	(2.97-6.09)	(3.62-7.47)	(10.4-13.7)
PCB (lip.)	ns	0.96	1.17	0.68	0.48
	-	(0.62-1.48)	(0.81-1.69)	(0.49-0.96)	(0.45-0.52)
bluntnose minnow					
sample size	6	4	5	5	5
body weight (g)	4.71	4.91	2.81	2.82	5.16
	(3.05-7.28)	(3.11-8.01)	(1.96-4.05)	(1.58-5.04)	(2.83-9.43)
lipid (%)	1.70	0.83	1.33	1.05	0.89
	(0.73-3.96)	(0.42-1.66)	(0.34-5.16)	(0.84-1.31)	(0.80-0.99)
PCB (w.w.)	29.0	9.78	6.24	10.4	7.96
	(20.5-41.1)	(7.35-13.0)	(4.44-8.76)	(6.84-15.8)	(6.39-9.92)
PCB (lip.)	1.71	1.13	0.45	0.99	0.89
	(0.69-4.22)	(0.67-1.91)	(0.11-1.89)	(0.67-1.46)	(0.71-1.13)
yellow perch (adult)					
sample size	5	5	5	5	5
body weight (g)	54.9	43.2	72.8	59.4	80.6
	(26.3-115)	(33.6-55.5)	(38.1-139)	(30.8-114)	(57.4-113)
lipid (%)	0.22	2.66	0.26	0.27	0.15
	(0.16-0.30)	(0.22-0.32)	(0.20-0.33)	(0.20-0.37)	(0.11-0.21)
PCB (w.w.)	9.08	11.4	8.76	8.43	4.98
	(5.76-14.3)	(5.66-23.0)	(5.73-13.4)	(4.55-15.6)	(3.47-7.16)
PCB (lip.)	4.16	4.26	4.29	3.14	3.31
	(2.53-6.82)	(2.14-8.45)	(2.77-6.64)	(1.80-5.47)	(2.06-5.31)

	Scugog	Boshkung	Wood	St. Nora	Opeongo
smallmouth bass					
sample size	5	4	5	5	5
body weight (g)	487	454	492	319[1]	153
	(212-111)	(197-1047)	(285-851)	(178-573)	(134-175)
lipid (%)	1.05	1.17	0.53	1.22	0.22
	(0.25-4.41)	(0.52-2.29)	(0.17-1.67)	(0.82-1.81)	(0.14-0.33)
PCB (w.w.)	7.47	25.5	6.17	35.4	4.77
	(5.38-10.4)	(17.5-37.2)	(4.54-8.39)	(18.8-66.6)	(4.14-5.49)
PCB (lip.)	0.71	2.42	1.16	2.91	2.20
	(0.21-2.42)	(1.56-3.76)	(0.49-2.75)	(1.58-5.36)	(1.61-3.02)
lake trout					
sample size	ns	5	ns	2	5
body weight (g)	ns	1241	ns	431	3060
	-	(625-2465)	-	(298-623)	(1824-5132)
lipid (%)	ns	4.36[1]	ns	0.71	2.33
	-	(2.98-6.3)	-	(0.56-0.89)	(1.59-3.41)
PCB (w.w.)	ns	68.5	ns	17.4	48.8
	-	(35.4-132.3)	-	(11.0-27.3)	(20.7-115)
PCB (lip.)	ns	1.55	ns	2.46	2.10
	-	(0.87-2.77)	-	(1.98-3.05)	(1.18-3.74)

1 mean value based on sample size of 4
2 mean value based on sample size of 3

Table 6 - Pooled values of lipid content and total PCB concentration (wet weight and lipid weight basis) for Boshkung, Wood, St. Nora and Opeongo lakes.

Taxa	Sample Size	Lipid content (%)	PCB concentration ($ng\ g^{-1}$ w.w.)	($ug\ g^{-1}$ lipid)
zooplankton	12	0.60 (0.22-1.63)	6.66 (2.57-17.2)	0.88 (0.62-1.25)
clam	20	0.27 (0.14-0.54)	5.41 (3.63-8.04)	1.78 (1.23-2.50)
golden shiner	16	0.92 (0.45-1.88)	6.25 (3.85-10.1)	0.77 (0.49-1.21)
bluntnose minnow	17	1.02 (0.52-1.99)	8.36 (5.81-12.0)	0.80 (0.35-1.85)
yellow perch	20	0.23 (0.16-0.33)	8.05 (4.48-14.5)	3.71 (2.20-6.25)
smallmouth bass	19	0.62 (0.23-1.68)	12.3 (4.65-32.6)	2.04 (1.06-3.95)
lake trout[1]	11	2.35 (1.12-4.94)	47.3 (20.6-109)	1.90 (1.12-3.24)

1 - sample taken from Boshkung, St. Nora and Opeongo, only.

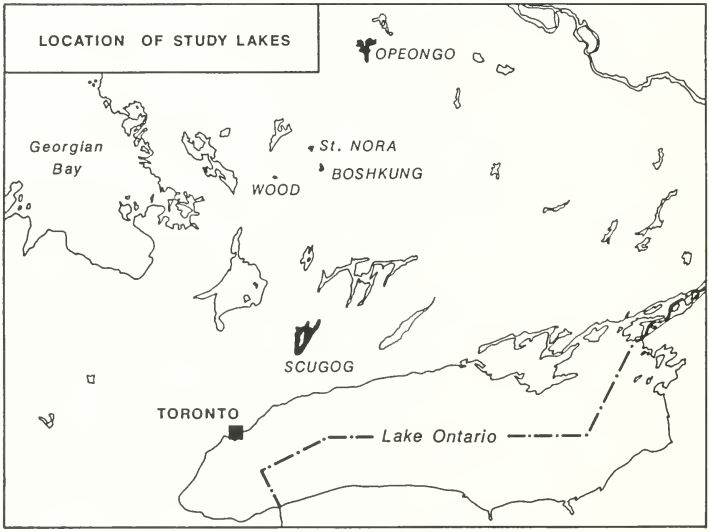

Figure 1: Location of the five study lakes in central Ontario.

Fig 2-Summary of the proportion of 19 individual congeners in 5 groups of biot and sediments in 4 study lakes. Samples sizes are given in Table 3 Maximum value of standard deviation of Lake Boshkung golden shiner is 56.

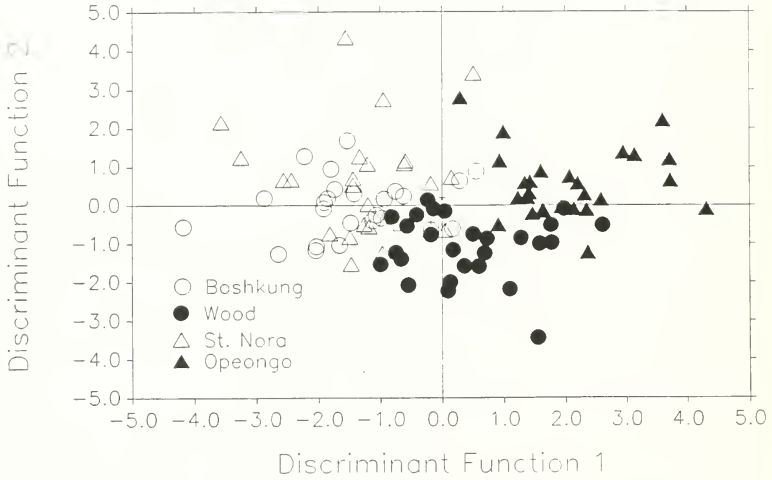

Figure 3: Characterization of differences in the pattern of PCB congeners in the four study lakes using two discriminant functions.

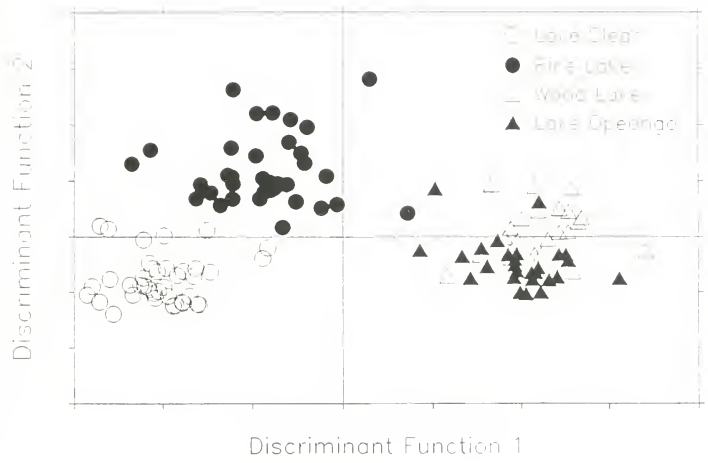

Figure 4: Characterization of differences in the pattern of PCB congeners using two discriminant functions for two lakes contaminated by atmospheric PCBs (Opeongo and Wood) and two lakes contaminated by point sources (Clear and Rice).

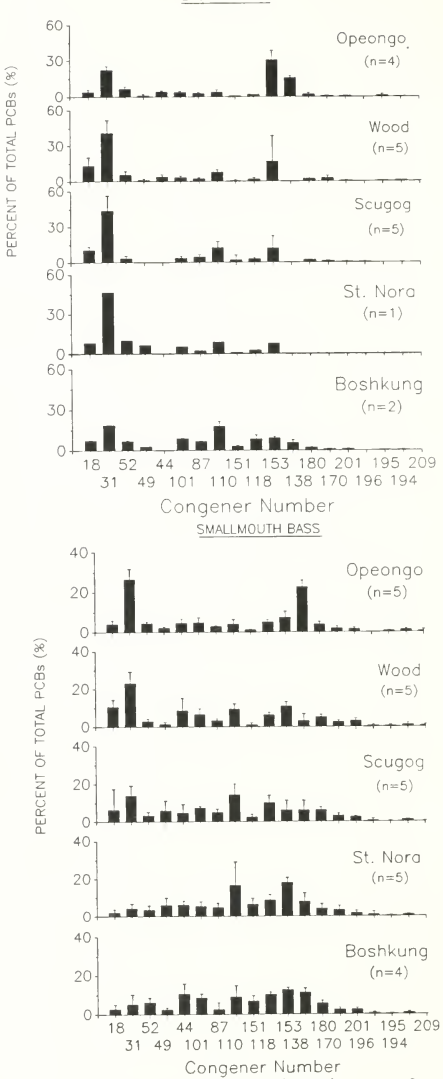

Figure 5 - Congener distribution in zooplankton and smallmouth bass in study lakes.

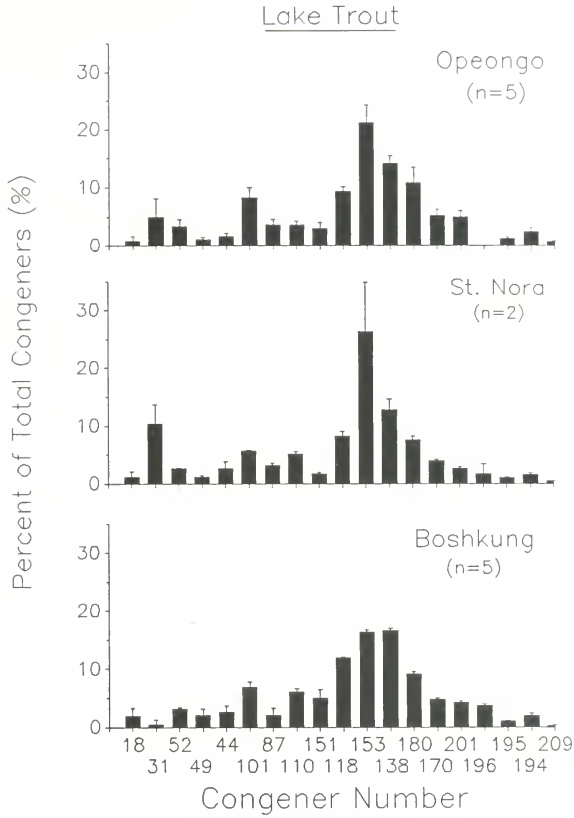

Figure 6 -Congener distribution in lake trout muscle from three study lakes. Co-eluting congeners have been removed from congener numbers for clarity.

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A Comparison of PCB Congener Distributions in Two Contaminated Lakes in Ontario

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ABSTRACT

PCB congener accumulation in biota and sediments involves several processes, including physical factors characterized by octanol-water partition coefficients and water solubility, and chemical factors which are influenced by the degree of chlorination and the substitution pattern of the individual congeners. The present study was conducted to determine if PCB congeners are distributed in a consistent pattern in two lakes known to have received point-source contamination with PCBs, and a control lake with no known point source. Samples of 4 groups of biota, water and sediment indicated that each lake had a unique pattern of congener distribution which was probably related to the source of the contamination. A comparison of total and individual PCB congener concentrations within each study lake showed that no one species consistently contained the highest residues of PCBs. Smallmouth bass had the highest concentration of PCBs in Rice lake while yellow perch was highest in lakes Clear and Scugog. Sediments contained lower concentrations of PCBs than biota and did not show enrichment of higher chlorinated congeners, despite having high organic carbon content. Within the contaminated lakes, YOY and older yellow perch had the same congener pattern, and there was no significant difference in their PCB concentration. This indicates that equilibrium concentrations of PCBs are established rapidly in the young fish and that all congeners equilibrate at the same rate.

INTRODUCTION

Many studies have focused on the distribution of PCBs (polychlorinated biphenyls) within lake ecosystems in an attempt to predict the factors influencing the accumulation of the PCBs by biota and sediments. Because of the low water solubility and lipophilic nature of PCBs, a strong relationship has been observed between the concentration of total PCBs and the lipid content of organisms within a particular lake (Oliver and Niimi 1988; van der Oost et al. 1988). The advent of high resolution capillary gas chromatography has shown that the factors controlling individual PCB congener distribution are much more complex than for PCB's as a group. Studies have attributed variations in congener bioaccumulation to stearic changes in the biphenyl molecule with

to predict the factors influencing the accumulation of the PCBs by biota and sediments. Because of the low water solubility and lipophilic nature of PCBs, a strong relationship has been observed between the concentration of total PCBs and the lipid content of organisms within a particular lake (Oliver and Niimi 1988; van der Oost et al. 1988). The advent of high resolution capillary gas chromatography has shown that the factors controlling individual PCB congener distribution are much more complex than for PCBs as a group. Studies have attributed variations in congener bioaccumulation to stearic changes in the biphenyl molecule with increased chlorination (Shaw and Connell 1984), differences in the rate at which an equilibrium is established between two phases for individual congeners (Oliver 1984; van der Oost et al. 1988) and differences in octanol-water partition coefficient (Oliver and Niimi 1988).

The interactions between the mechanisms controlling PCB congener bioaccumulation are also reflected in whole lake studies. Oliver and Niimi (1988) found a constant pattern of PCB congeners in the upper trophic levels within Lake Ontario and reported a good relationship between the partition coefficient of individual congeners and their bioaccumulation factor (BAF). Van der Oost et al. (1988) suggested that the congener distribution in a particular trophic level was better described as a function of the length of time available to accumulate the contaminants (i.e. age of the organism) than simple partitioning between water, sediment and biota; consistent with the model of Weininger (1978). Therefore, the distribution of PCB congeners within any particular aquatic organism in a given lake is probably the result of complex interactions between the congener composition of the original PCB source, removal and transport mechanisms within the lake, chemical and physical properties of the congeners which affect uptake into the organism, the route of exposure (i.e diet or water borne) and the exposure period (i.e. age of the organism).

The present study was conducted to compare the distribution of 19 PCB congeners through the water, sediments and biota in three lakes, two of which have been contaminated with PCBs from point sources. These lakes are similar with respect to size, trophic status and food web structure, but differ with respect to the source of PCBs. Lake Clear was contaminated by oiling of a roadway along the northwest rim of the lake in the mid to late 1970's. This resulted in concentrations of PCBs exceeding 2 $\mu g\ g^{-1}$ in lake trout (Salvelinus namaycush Walbaum) in 1981 (Ontario Ministry of the Environment, unpublished data). Rice Lake was contaminated by

inputs from industries in Peterborough, Ontario over a number of years. Scugog Lake is similar to Rice Lake in size and trophic status, but monitoring by low resolution gas chromatography has shown the total PCB concentration in fish muscle to be below detection limits (<20 ng g^{-1}). Hence it is assumed that the major source of PCBs to Lake Scugog is through the atmosphere (Strachan and Eisenreich 1988).

It is our primary goal to test if there are consistent relationships in all three lakes between PCB congener distribution and trophic level. Analysis of PCB distributions in biota will focus primarily on four species (smallmouth bass, yellow perch, crayfish and zooplankton) which are common to all three lakes. Our hypothesis is that, although the dominant congeners within the lakes will be different, the relative accumulation of the individual congeners through the trophic levels will occur in a consistent manner, possibly as a function of partition coefficient of the congeners. This should be evident by the enrichment of higher chlorinated congeners in compartments with high lipid levels (i.e. biota with high fat content) or organic carbon levels (i.e. sediments). It is also our intent to use the PCB congener distribution data to draw tentative conclusions regarding the potential for reductions in the PCB levels in the upper trophic levels (e.g sport fish).

MATERIALS AND METHODS

Collection of Samples

Samples of biota and sediments were collected in October 1986 and June 1987 in all three lakes. Crayfish (Procambarus sp.) were collected using hand held dip nets and strainers. Zooplankton were collected using a 0.25 m^2 conical net made of canvas, 276 μm mesh nytex mesh and brass cod bucket. Tows were made for approximately 5 minutes at a depth of 5 m and the plankton collected in 2-3 tows grouped to give one sample. The plankton were further concentrated by passing the sample through 64 μm mesh.

Adult yellow perch (Perca flavescens Mitchell) and smallmouth bass (Micropterus dolomieui) were collected using a 20 m bag seine or a 1.3 or 2.6 m trap net. YOY yellow perch were collected using a 20 m bag seine. Except for the trap nets, all sampling equipment was soaked in reagent grade methanol prior to sampling. Total body

weight and length of all fish were measured in the field prior to dissection and freezing. Samples of larger fish were dissected soon after capture and frozen in solvent washed aluminum foil. A section of muscle tissue was taken from the dorsal area of the fillet below the dorsal fin for smallmouth bass and adult yellow perch samples. With YOY perch, the head, tail and internal organs were removed before analysis. Crayfish samples consisted of muscle dissected from the tail.

Sediment cores were collected using a K-B corer, with brass tubes 0.35 m in length. After collection of the core, a plug was inserted into the bottom of the brass tube and the core elevated in increments of 3 cm. The individual 3 cm sections were collected in an aluminum sectioning device which was cleaned between samples. The sections were stored separately in clean, solvent washed 250 ml Mason jars. Sediments samples for total organic carbon were collected by Ekman Grab and analyzed by the Ontario Ministry of the Environment in Rexdale, Ontario (Ontario Ministry of the Environment 1983). Total organic carbon was determined by measurement of carbon dioxide gas generated during high temperature combustion.

Water samples were collected by passing 18 L of lake water through 137 mm diameter organic binder-free filters (pore size of 0.3 μm) and extracting the water with two volumes (500 and 400 ml) of distilled in glass dichloromethane. Volumes of dichloromethane were added to the water sample in a 20 L stainless steel extraction vessel, stirred for 15-20 min and removed by displacement using nitrogen gas. The 0.3 μm filters were stored in solvent washed 250 ml Mason jars with approximately 100 ml of dichloromethane until extraction.

Upon collection, all samples were stored temporarily in 250 or 500 ml Mason jars which had been washed with reagent grade acetone and pesticide grade hexane, and covered with solvent washed aluminum foil. Except for zooplankton, total body weight and length of organisms were measured in the field prior to dissection and freezing. All samples were frozen within 8 hours of collection and remained frozen until analysis.

Sample Preparation and Analysis

Sediment samples of approximately 5 g were prepared for analysis according to method "A" of the Ontario Ministry of the Environment (OME, 1983). Briefly, sediments were extracted with acetone by sonication, and back-extracted into methylene chloride.

The extract was dried by passing through sodium sulphate and rotary evaporated to 2 ml for sample cleanup and fractionation. Samples were cleaned up and fractionated into three subfractions by column chromatography (1 cm i.d.) on 5 g of activated silica gel (60-200 mesh). The column was eluted with 10 ml of hexane to yield Fraction A (PCBs, DDE, aldrin, lindane, heptachlor, and mirex), and the column was subsequently eluted with 40 ml of 25% methylene chloride in hexane, and 40% methylene chloride in hexane to yield organochlorine pesticide subfractions B and C, respectively. Sulphur compounds were removed from Fraction A by precipitation with mercury.

Biota samples of approximately 5 g were ground with sodium sulphate in a mortar, and extracted into hexane with a soxhlet apparatus for 1 h. A subsample of the extract was rotary evaporated to 2 ml and made up to 5 ml in 55:45 hexane:methylene chloride. Lipids were removed from this extract by gel permeation chromatography on a 1 cm i.d. X 28 cm column of Biobeads SX2 (200-400 mesh). The column was eluted at a rate of 2 ml per minute with 55:45 hexane:methylene chloride. The first 90 ml of eluent, which contained lipid, was collected and evaporated to dryness for gravimetric determination of lipid content. The next 100 ml of eluent, which contained PCBs and organochlorine pesticides, was collected and subjected to further cleanup before analysis. The extract was cleaned up and fractionated by silica gel column chromatography, as described for the sediment extracts.

The methylene chloride collected in the field for analysis of PCBs in water was passed through sodium sulphate and rotary evaporated to 2 ml. The extract from two 18 L samples was pooled, and then partitioned into hexane by successive additions of hexane and evaporation under nitrogen. The sample was then cleaned up and fractionated by silica gel chromatography, as described above. The glass fibre filters containing suspended particulate material were manually broken up while immersed in the methylene chloride originally added in the field. The entire sample was filtered under suction through sodium sulphate in a Buchner funnel. A further 150 ml of methylene chloride was then passed through the filter. The extract was partitioned into hexane and cleaned up/fractionated by silica gel chromatography, as described previously.

Samples were analyzed for PCBs by high resolution gas chromatography on a Varian 3500 gas chromatograph with ECD, using a 30 m DB5 capillary column (250 μm OD, 25 μm ID) and splitless injection. The flow of hydrogen carrier gas was 1.8 ml/min and the

flow of nitrogen make-up gas into the detector was 28 ml/min. GC conditions were: injector 250°C, detector 275°C, and initial column temperature 80°C. The column temperature was programmed as follows: 1 minute hold time at 80°C, increase at 4°/min to 160°C, increase at 1.5°/min to 230°C, increase at 7°/min to a final temperature of 250°C, with a final hold time of 20 min. Individual congeners were identified by retention time (window 0.02 %), and quantified from integrated peak areas. Detection limits for individual congeners varied from 0.02 to 0.04 ng/ml.

Quantification of individual PCB congeners was made by comparison to standards purchased from the National Research Council in Halifax, Canada. The standard was a mixture of the NRC standards CLB-1 A and D, to which congener 52 (2,2',5,5') was added. DDE was added as a relative retention time marker. Nineteen congeners were chosen for analysis (Table 1), the sum of which represented 46%, 53%, and 62% of the total PCBs present in Aroclors 1242, 1254, and 1260, respectively (Murphy et al. 1987).

Of the 19 congeners quantified from the standard, 4 of the congeners coeluted with other PCB congeners present in environmental samples (Table 1). All coeluting peaks were reported as the concentration of the congener present in the standard, with the exception of congener 77 which coeluted with congener 110. Since congener 77 (3,3',4,4') makes up a very small proportion of PCBs in commercial Aroclors in comparison to congener 110 (2,3,3',4',6), it was assumed that no congener 77 was present in the samples. Since there are no purified standards of congener 110 available, congener 77 in the standard was used as a retention time marker for 110 and was used to calculate concentrations of 110 in Lake Clear samples. The integrated area of the peak eluting at the retention time for 77 was multiplied by the response factor for congener 77 times the ratio of the relative response factors for congeners 77 and 110, as determined by Mullin et al. (1984).

Data Treatment and Statistical Analysis

The relative proportion of each congener was calculated by dividing the wet weight concentration of the congener by the sum of all 19 major congeners. Data were analyzed using the personal computer version of SPSS software (SPSS/PC, Inc., Chicago, Ill. 1988). Significant differences were measured at the 0.05 level (i.e. $P<0.05$). All means and range tests were calculated using log transformed data to normalize the residuals. Discriminant function analysis was conducted using SPSS/PC and Statgraphics. Random

numbers between 0 and the detection limit were entered for all zero (undetectable) values. Congener 209 (decachlorobiphenyl) was removed prior to discriminant analysis because of the large number of zero values.

RESULTS

Morphometric and water chemistry data is given for all three study lakes in Table 2. Rice and Scugog lakes are similar with respect to surface area and mean depth and in the water quality parameters of pH and alkalinity. Dissolved organic carbon (DOC) and total suspended solids are highest in Lake Scugog (8.7 and 24 mg L^{-1}) but are also relatively high in Rice Lake (5.2 and 7.8 mg L^{-1}) and Lake Clear (2.8 and 1.1 mg L^{-1}), respectively.

PCB concentrations in water and suspended solids were similar between Lake Clear and Rice Lake, but were considerably higher than in Lake Scugog. Total congener concentrations in the water were 1.92 ng L^{-1} (SD=0.40, n=2) in Lake Clear and 2.85 ng L^{-1} (SD=0.49, n=3) in Rice Lake, but only 0.89 ng L^{-1} (SD=0.32, n=2) in Lake Scugog. Similarly, PCB concentrations on suspended particulates were 870 (SD=35.4) and 1078 (SD=289) ng g^{-1} dry weight in Lake Clear and Rice Lake, respectively, and 49.2 (SD=11.9) in Lake Scugog.

The geometric means of body weight, lipid content and PCB concentration on a wet weight and lipid weight basis for the biota, and organic carbon content and PCB concentration on a dry weight and organic carbon basis for the sediment samples collected in all three test lakes are listed in Table 3. The results of the statistical comparison of the means using Scheffe's range test are shown in Table 4. Means which are not statistically significant are indicated by a bar in the respective columns while significant differences ($P<0.05$)are indicated by asterisks. Age estimates from scales indicated that the adult perch and bass samples collected in all three lakes were approximately 3-4 years old; except for the Rice Lake bass, which were approximately 5-6 years.

During the original sample collection, uniform sizes of biota were intentionally collected from all three lakes. As a result, it is not surprising that body weight and lipid contents are similar for all three lakes, while PCB concentrations are significantly higher in the contaminated lakes. For example, body weight and lipid content (approximately 0.5-1.0% lipid) of the smallmouth bass samples are similar in all 3 lakes, but PCB residues are significantly higher on both a wet weight and lipid weight basis

in Lake Clear and Rice Lake. Sediments show essentially the same trend, with dry weight concentrations in Rice Lake and Lake Clear being not significantly different from each other, but both being significantly greater than in Lake Scugog. On an organic carbon basis, however, the concentration is highest in Lake Clear, followed by Rice Lake and then Scugog. There is no significant correlation between lipid content and PCB concentration (wet weight) between lakes for any of the 5 species of biota, except for zooplankton, which had a correlation coefficient of 0.614.

YOY perch (i.e <1 y) data are included in Table 3 for comparison with older perch (>1 y) in lakes Rice and Clear. In both lakes, there was no significant difference in total PCB congener concentration (both wet weight and lipid weight basis) between the samples of younger and older perch.

There were no consistent trends between lipid content of biota and PCB concentration, or between trophic level or ecological niche and PCB concentration within any of the study lakes. For example, in Rice Lake, smallmouth bass had the highest PCB concentration on both a wet weight and lipid basis, followed by bluntnose minnow, and was significantly higher than the perch sample on a lipid weight basis. In Scugog Lake, however, smallmouth bass had the lowest PCB concentrations on a wet weight basis, and had low PCB levels on a lipid weight basis, although not significantly different from any other biota samples.

The proportion of individual congeners changes in biota between lakes and, to some extent, between trophic levels (Fig. 1). The dominant congeners in Rice Lake cover a broad range of tri- to hexachlorobiphenyls (congeners 18 to 138). The more water soluble congeners (18 to 44) are proportionately higher in water and sediment than in the upper trophic levels, which show a relatively even distribution of the full spectrum of tri- to hexachlorobiphenyls. Congeners 101, 110, 118(149) and 153(132) comprise a substantial proportion of the PCBs in crayfish, yellow perch and smallmouth bass samples. Dominant congeners in almost all Lake Clear samples were the pentachlorobiphenyl congeners 101, 110 and 118, and the hexachlorobiphenyl congeners 153(132) and 138 (Fig 1). The one exception is the water samples which contained a higher proportion of less chlorinated congeners.

The differences in congener patterns between trophic levels are extensive in Lake Scugog. The lower chlorinated congeners are dominant in sediments, crayfish and zooplankton, with congeners 18, 31(28) and 52 comprising approximately 40-60% of total PCBs. In the yellow perch and smallmouth bass samples, there is a more even

distribution of congeners which includes equal portions of tri- to hexachlorobiphenyl congeners. The water samples also show a broad range of congeners, with tri- to hexachlorobiphenyls each accounting for 10-15% of the total PCB.

The statistical significance of these changes in congener distribution was tested using discriminant analysis. Data on the proportion of each PCB congener in the four species of biota, water and sediments were entered as a matrix. Discriminant analysis was used to separate the data according to i) the lake from which the sample was collected, or ii) the sample type (i.e. sediment, zooplankton, etc.). The analysis differentiated samples from the individual lakes with two functions which accounted for 79% and 21% of the variance, respectively, and correctly classified 96% of the samples to the appropriate lake (Fig 2). Lake Scugog was separated by the first discriminant function, which accounted for the majority of variance, on the basis the trichlorobiphenyl congeners 18 and 31(28) and the octachlorobiphenyl 201. Lake Clear was separated on the basis of three congeners, the pentachlorobiphenyl congeners 101 and 87 and the coeluting penta- and hexachlorobiphenyl congeners 118 and 149. The second discriminant function separated Rice Lake by the high proportion of tetrachlorobiphenyls 52, 44 and 49, and Lake Clear and Lake Scugog by the high proportions of hexachlorobiphenyl 138 and heptachlorobiphenyl 170.

Separation of biota, sediments and water by discriminant analysis using data pooled from all three lakes was less definitive (Fig 2). The six groups were differentiated with 5 functions, the first two of which accounted for only 53% of the total variability. Between 90 and 100% of the sediment and crayfish samples were properly classified, however, only 60-70% of the zooplankton, perch and bass were correctly classified. The highest loadings in the first discriminant function were from congeners 118, 49 and 31(28).

DISCUSSION

A complex series of chemical and physical interactions govern the transport and distribution of PCBs within lakes, including adsorption by suspended particulates (Thomann and Di Toro 1983; Opperhuizen and Stokkel 1988), dissolved organic matter which may influence water solubility (Gschwend and Wu 1985; Sawhney 1987) and colloidal material (Baker et al. 1986). Water quality and morphometric data for Rice Lake and Lake Scugog show that the two

lakes are similar in a number of respects, but particularly with regard to the water quality parameters which influence PCB transport. Both lakes are shallow, highly eutrophic and productive, possess high levels of DOC (dissolved organic carbon) and TSS (total suspended solids) in the water, and high organic carbon content in the sediments (18 and 12%, respectively). In contrast, Lake Clear has lower concentrations of DOC and TSS, is presumably less eutrophic, and has a maximum depth considerably greater than the other two lakes. The extensive hypolimnion in Lake Clear would permit suspended solids to settle to the bottom, and would inhibit resuspension of bottom sediment. Hence it is expected that PCB transport mechanisms are similar in Lakes Scugog and Rice, and different from Lake Clear.

The lakes are notably different with respect to the major sources of PCBs. The contamination of Lake Clear occurred in the mid to late 1970's, when a PCB mixture similar to Aroclor 1254 was applied as a dust suppressant to a road along one side of the lake. The source of the contamination was removed some time later, but a significant amount of the PCBs remain in the lake. The sources of PCBs to the other lakes are less certain. Since the 1950s, a range of Aroclor mixtures (e.g. Aroclor 1242, 1248, 1254, 1260) appear to have entered Rice Lake and its watershed from local industrial sources, although the specific rates of input are unknown. Lake Scugog has no known point source of PCBs. Hence, it is assumed that atmospheric deposition is responsible for the bulk of PCBs in the lake. Atmospheric deposition has been shown to be responsible for up to 90% of the PCBs in Lake Superior and approximately 60% in Lakes Huron and Michigan (Strachan and Eisenreich 1988).

These differences in the sources of PCBs are evident in the patterns of congeners present in the 3 lakes. Virtually all samples collected in Lake Clear, with the exception of water and suspended solids, showed a distinctive pattern of congeners which is very similar to Aroclor 1254. Metcalfe and Macdonald (1990) used principal component analysis to show that this pattern was consistent through all biota and sediment samples. In the present study, discriminant analysis separated Lake Clear from the other lakes on the basis of the proportion of congeners 101, 87 and 118; all of which are dominant congeners in Aroclor 1254 (Murphy et al. 1987).

Samples from Rice and Scugog lakes show a much more even distribution of PCB congeners than the pattern of primarily tetra- to hexachlorobiphenyl congeners observed in Lake Clear. Both lakes

contain tri- to hexachlorobiphenyl congeners, although the proportion of the individual congeners is different between the biotic and abiotic compartments. In general, Scugog contains a higher proportion of less chlorinated congeners (>50% of total congeners in some samples) than either of the two contaminated lakes. This is consistent with the assumption that atmospheric deposition is the dominant source of relatively volatile PCB congeners in this lake. Swackhamer et al. (1988) estimated the atmospheric input of PCB congeners to isolated lakes in Wisconsin and found that a larger proportion of lower chlorinated congeners (18, 101, 52) entered the lake relative to higher chlorinated congeners. Several studies have shown that less chlorinated congeners are transported in the vapour phase in the atmosphere (Duinker and Bouchertall 1989), presumably because of their higher volatility (Shiu and Mackay 1986). The successful separation of Lake Scugog from the other lakes by discriminant analysis, on the basis of the trichlorobiphenyls 18 and 31(28), supports the observation that the less chlorinated congeners are the dominant congeners in the lake. This analysis shows that each of the three lakes used in this study each contains a unique set of congeners.

The total PCB concentration of all samples collected from the two contaminated lakes are higher than the control lake. However, the distribution of the compounds between biotic and abiotic compartments in the lakes does not follow expected patterns. It was expected that the lake sediments would be highly efficient at absorbing these hydrophobic contaminants (Steen et al. 1978; Karickhoff 1981; Formica et al. 1989), particularly because of their high organic carbon content. The data in Table 3, however, show that the sediments in the study lakes are not efficient at accumulating either PCBs as a group, or the more hydrophobic congeners, in particular. In all three lakes, the sediments had lower PCB concentrations (organic carbon basis) than biota (lipid basis). This is surprising, since several authors have indicated that adsorption of the PCBs onto suspended solids, with subsequent deposition into the sediment is a major mechanism controlling PCB transport in aquatic systems (Thomann et al. 1987; Formica et al. 1989). Suspended solids in the contaminated lakes have considerably higher PCB concentrations than the control lake, which indicates that adsorption of PCBs by the suspended particulates is occurring, and that the concentration is directly related to the amount of PCB in the lake system. However, the low concentrations of PCBs in the bottom sediments, relative to the biota, supports the conclusion that the mechanism is not particularly efficient, even with 18%

organic carbon content, and that a high proportion of PCBs are available for accumulation in the biota.

It is also interesting that there is no enrichment of the higher chlorinated congeners in the sediments, although these compounds are present in the lake. In fact, the reverse appears to be true in Rice and Scugog Lakes where there is a higher proportion of less chlorinated congeners in sediments than in the upper trophic levels. The reason for the lack of partitioning of the higher chlorinated congeners into sediments is not readily apparent, since the congeners are highly hydrophobic. One factor which may influence the partitioning of the higher chlorinated congeners into the sediments is the presence of high concentrations of dissolved organic matter in Rice Lake and Lake Scugog. DOC has been shown to increase the solubility of PCBs in water (Gschwend and Wu 1985), and the high levels observed in Rice and Scugog could decrease the amount adsorbed onto the sediments. If so, then the mechanisms controlling PCB transport in eutrophic lakes could be different from those in oligotrophic lakes.

It is surprising that there were no clear relationships between the PCB concentrations in the lake biota and either trophic level, ecological niche, or lipid content of the organisms. In the two contaminated lakes, smallmouth bass had the highest total PCB concentration (wet weight) of all biota, although only in Rice Lake is it statistically significant. In lakes Clear and Scugog, crayfish and yellow perch had the highest concentration of PCBs on a lipid basis, although the variability was high, and the differences were not statistically significant. Oliver and Niimi (1988) observed a direct relationship between PCB concentration and lipid content in the biota of Lake Ontario, where the highest lipid and PCB concentrations were found in the highest trophic levels (i.e. lake trout). A similar relationship was noted by van der Oost et al. (1988), where the highest trophic level, the eel (Anguilla anguilla), contained the highest lipid content (14.9%) and also the highest PCB concentration. Both of these latter studies are consistent with the view that there is a direct correlation between the partition coefficient of a compound and its potential to accumulate in the lipids of biota (Kenaga and Goring 1980; Mackay 1982). The reason for the lack of a relationship in the present study may be related to the similarity in the lipid content of the organisms within the lakes (i.e. no significant differences within the biota of Rice Lake). The data presented here demonstrates that no particular group consistently accumulates higher amounts of PCBs in all three lakes, and that the potential for bioaccumulation does

not necessarily differ between benthic and pelagic organisms. Thus, the concept of biomagnification of lipophilic compounds through the trophic levels of lakes may be based on observations of high residue concentrations in a few species of top predators which happen to have high lipid contents (e.g. lake trout, eels).

This lack of consistent trends in PCB accumulation within the biota of the lakes is also seen when making comparisons of congener patterns. Higher proportions of the lower chlorinated congeners are present in the water phase of both contaminated lakes (but not in Lake Scugog), and in the lower trophic levels and sediments of lakes Rice and Scugog. Smallmouth bass and perch in Rice Lake and Lake Scugog show a broad range of congeners, unlike Lake Clear which shows predominantly penta- and hexachlorobiphenyl congeners. The lack of consistent patterns over the three lakes is shown in the discriminant analysis, where the upper trophic levels could not be successfully classified by group on the basis of 5 discriminant functions. Therefore, based on the small sample size of 3 lakes, we must reject the hypothesis that congener partitioning within the lakes is the same for contaminated and clean lakes, and conclude that the complex series of interactions, biotic and abiotic, which influence PCB accumulation are probably specific for each lake. Hence, each lake must be considered independently. Again, this is consistent with van der Oost et al. (1988), who concluded that the distribution of each congener must be studied separately. This implies that it may not be possible to estimate the concentration of either total PCB or specific toxic PCB congeners (Kannan et al. 1988; Niimi and Oliver 1988; Niimi and Oliver in press) in sport fish based on the concentration of PCBs in a single monitoring species. The inconsistent relationships between hydrophobicity and accumulation observed in the present study suggest that sampling of many groups of biota within each lake are necessary to establish a full picture of the distribution of the contaminants within the lake.

The rate of disappearance of PCBs in the contaminated lakes has significant ramifications for the fisheries in the lakes. The total PCB concentration in YOY to yearling yellow perch is declining near the area of contamination in Lake Clear, probably as a result of deposition of the PCBs into the lake sediments (Metcalfe and Macdonald, 1990). There is little evidence for losses of the contaminants by either volatilization (Swackhamer and Armstrong 1986) or microbial degradation (Brown et al. 1987). Comparison of the Lake Clear and Rice Lake yearling perch data (Fig. 3) indicates that total PCB concentration in the Rice Lake

perch is constant over time, unlike Lake Clear. The broken symbols in Figure 3 are whole body total PCB estimates calculated from the YOY muscle values reported in Table 3. The conversion was made using the muscle/whole body concentration ratio of 2.5 (Niimi and Oliver 1983) and by assuming that the 19 major congeners analysed in this study account for approximately 50% of total PCBs (Murphy et al. 1987). The constant concentration in the Rice Lake yearling perch indicates that PCBs are available to the biota in approximately the same amounts as in 1977. This may be the result of the shallow depth of Rice Lake, which allows the resuspension of PCBs in the sediments, or continued contamination from the original source. Ferguson and Metcalfe (in press) concluded that particle bound PCBs are being continually added to Rice Lake from the contaminated Otonabee River.

Comparison of the total PCB and congener pattern in the YOY and older perch samples (Fig. 4) suggests that the concentration of the PCBs in biota reaches equilibrium rapidly, relative to the age of the organism. There was no significant difference in total PCB congener concentration on either a wet weight or lipid weight basis between the two perch age groups in Rice Lake and Lake Clear, and a strong similarity in congener patterns between the two age groups within each lake. For example, in Rice Lake, YOY and adult perch show an almost identical pattern of congeners, except for a higher proportion of 31(28) in the younger fish. This higher proportion of the less chlorinated congener in the YOY sample could be the result of feeding on zooplankton, which also had a high proportion of congeners 31(28). In Lake Clear, virtually the same pattern of congeners is observed in YOY and adult perch samples. These similarities between fish which are 1 month old and 3-4 years old indicates that the PCB uptake occurs rapidly in the young fish, and equally for all congeners.

This study shows that the distribution of PCB congeners in small contaminated lakes does not occur in a consistent, predictable manner, although there are some indications of an increase in the proportion of higher chlorinated congeners in higher trophic levels. Although adsorption by suspended solids is occurring in all three study lakes, the transport of the PCBs to the sediment by this process does not seem efficient. Thus, PCBs in these lakes may be available to biota for long periods of time. The similarity in congener patterns and total PCB concentration in two age groups of yellow perch in the contaminated lakes suggests that biota accumulate PCBs rapidly from their environment, and that equilibrium between the organism and its environment is established

rapidly. Therefore, the management strategy of stocking fast-growing fish to maintain low PCB body burdens in contaminated lake systems will probably have limited success.

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Table 1 - Summary of the PCB congener IUPAC numbers, chlorine substitution and octanol-water partition coefficients (log Kow) analysed in samples from Scugog, Rice and Clear lakes.

Congener Number[1]	Chlorine Number	log K_{ow}[2]	Chlorine Position
18	3	5.24	2,2',5
31(28)	3(3)	5.67(5.67)	2,4',5 (2,4,4')
52	4	5.84	2,2',5,5'
49	4	5.85	2,2',4,5'
44	4	5.75	2,2',3,5'
101	5	6.38	2,2',4,5,5'
87	5	6.29	2,2',3,4,5'
110(77)	5(4)	6.48(6.36)	2,3,3',4',6 (3,3',4,4')
151	6	6.64	2,2',3,5,5',6
118(149)	5(6)	6.74(6.67)	2,3'4,4',5 (2,2',3,4',5',6)
153(132)	6(6)	6.92(6.58)	2,2',4,4',5,5' (2,2',3,3',4,6')
138	6	6.83	2,2',3,4,4',5'
180	7	7.36	2,2',3,4,4',5,5'
170	7	7.27	2,2',3,3',4,4',5
201	8	7.62	2,2',3,3',4,5,5',6'
196	8	7.65	2,2',3,3',4,4',5,6'
195	8	7.56	2,2',3,3',4,4',5,6
194	8	7.80	2,2',3,3',4,4',5,5'
209	10	8.18	2,2',3,3',4,4',5,5',6,6'

[1] - IUPAC numbering system for PCB congeners.
[2] - Log K_{ow} values from Hawker and Connell (1988).

Table 2 - Lake morphometry and water quality data for the three study lakes. DOC, pH and alkalinity are the means of 5 samples, while TSS (total dissolved solids) are the means of 10 samples.

	Clear	Rice	Scugog
Surface area (Ha)	1727	9156	8256
Mean Depth (m)	11.0	2.5	1.4
Maximum Depth (m)	43.0	13.0	7.6
pH	8.4	7.4	8.2
alkalinity (mg $CaCO_3$ L^{-1})	111.2	98.9	128.0
DOC (mg L^{-1})	2.8	5.2	8.7
TSS (mg L^{-1})	1.1	7.8	24.0
Sediment organic carbon content (%)	11.2	18.0	12.0

Table 3 - Geometric means and standard deviations (in brackets) of body weight, lipid content, and PCB concentration for biota samples collected from Lake Clear, Rice Lake and Lake Scugog. PCB concentration and organic carbon content are given for the sediment samples from each lake.

Group	Sample Size (n)	Body Weight (g)	Lipid (%)	PCB Concentration wet weight (ng g^{-1})	PCB Concentration lipid weight ($\mu g\ g^{-1}$)
Lake Clear					
sediment	5	-	-	571[1] (410-796)	5.35[2] (4.19-6.82)
crayfish	5	20.9[3] (11.2-39.0)	0.19 (0.10-0.35)	73.2 (38.0-141)	39.1 (11.8-130)
zooplankton	5	-	1.17 (1.00-1.38)	59.3 (47.7-73.9)	5.06 (4.51-5.68)
yellow perch					
YOY	5	2.74 (1.94-3.87)	0.48 (0.36-0.64)	89.8 (79.3-102)	18.9 (13.0-27.4)
adult	15	67.7 (22.5-204)	0.22 (0.17-0.28)	76.3 (47.7-122)	35.1 (21.3-57.7)
smallmouth bass	5	720 (682-760)	0.75 (0.59-0.97)	153 (125-186)	20.2 (16.7-24.5)
Rice Lake					
sediment	5	-	-	359[1] (234-552)	1.99[2] (1.30-3.06)
crayfish	5	8.11 (4.66-14.1)	0.20 (0.19-0.22)	7.98 (3.71-17.2)	3.94 (1.90-8.19)
zooplankton	5	-	0.17 (0.13-0.21)	28.8 (27.0-30.7)	17.0 (14.2-20.5)
yellow perch					
YOY	5	7.24 (6.62-7.91)	0.43 (0.28-0.64)	27.0 (19.1-38.3)	6.33 (3.67-10.9)
adult	11	21.7 (6.81-69.5)	0.41 (0.20-0.84)	36.2 (22.5-58.4)	8.81 (4.17-18.7)
smallmouth bass	5	286 (244 - 335)	0.48 (0.15-1.51)	146 (101 - 211)	30.9 (9.14-104)
Lake Scugog					
sediment	5	-	-	22.2[1] (20.6-23.9)	0.14[2] (0.12-0.16)
crayfish	5	28.0 (20.4-38.5)	0.26 (0.13-0.49)	8.48 (2.84-25.3)	3.32 (1.04-10.6)
zooplankton	5	-	0.22 (0.17-0.27)	2.73 (2.02-3.71)	1.27 (0.79-2.03)
yellow perch	5	54.9 (26.3-115)	0.22 (0.16-0.30)	9.08 (5.76-14.3)	4.16 (2.53-6.82)
smallmouth bass	5	487 (212-1120)	1.05 (0.25-4.40)	7.47 (5.38-10.4)	0.71 (0.21-2.42)

1 - concentration is ng g^{-1} dry weight
2 - sediment concentration is calculated on an organic carbon basis
3 - mean values based on sample size of 4

Table 4 - Statistical comparison of geometric means of body weight, lipid content and PCB concentration on a wet weight (w.w.) and lipid weight (lip.) basis using Scheffes multiple comparison. Different letters in two columns for any sample denotes that they are significantly different ($P<0.05$). The same letter in two columns indicates no significant difference.

	Clear	Rice	Scugog
sediment			
PCB (dry w.)	a	a	b
PCB (org. C)	a	b	c
zooplankton			
lipid content	a	b	b
PCB (w.w.)	a	b	c
PCB (lip.)	a	b	c
crayfish			
body weight	a	a,b	b
lipid content	a	a	a
PCB (w.w.)	a	b	b
PCB (lip.)	a	b	b
yellow perch			
body weight	a	b	a,b
lipid content	a	b	a,b
PCB (w.w.)	a	b	c
PCB (lip.)	a	b	b
smallmouth bass			
body weight	a	b	a,b
lipid content	a	a	a
PCB (w.w.)	a	a	b
PCB (lip.)	a	a	b

Figure 1 - Congener patterns for sediment, water and 4 species of biota from the three study lakes. The numbers along the bottom of each graph are the IUPAC numbers for each congener, as reported in Table 1. Each bar in the histogram represents the percent of the total of the 19 congeners quantified in the samples. The error bars indicate one standard deviation about the mean.

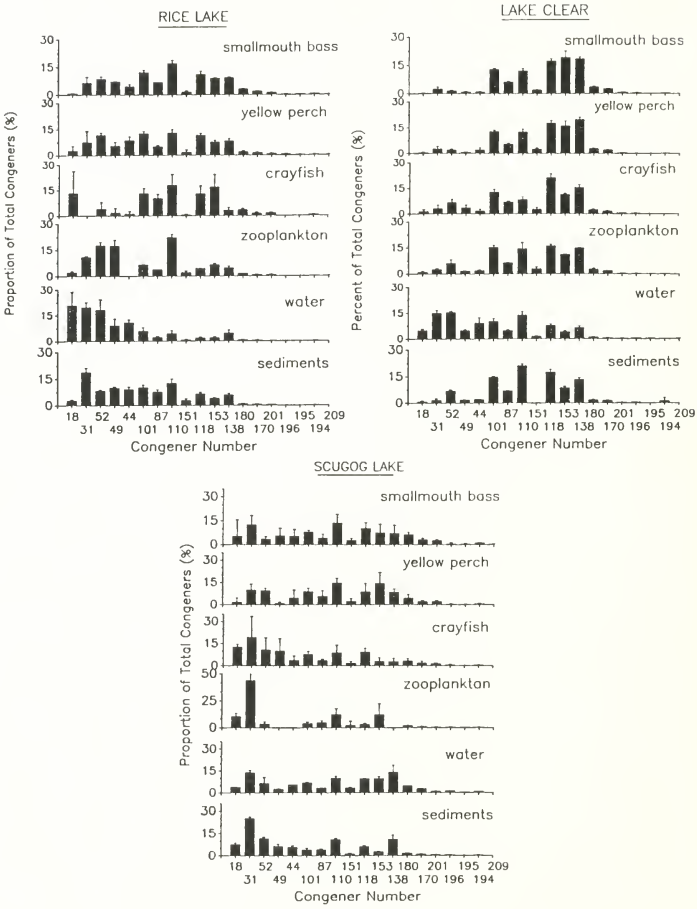


Figure 2 - Discriminant analysis of proportional data by lake (A) and by species (B). Circled areas denote the majority of samples for a particular lake or sample type.

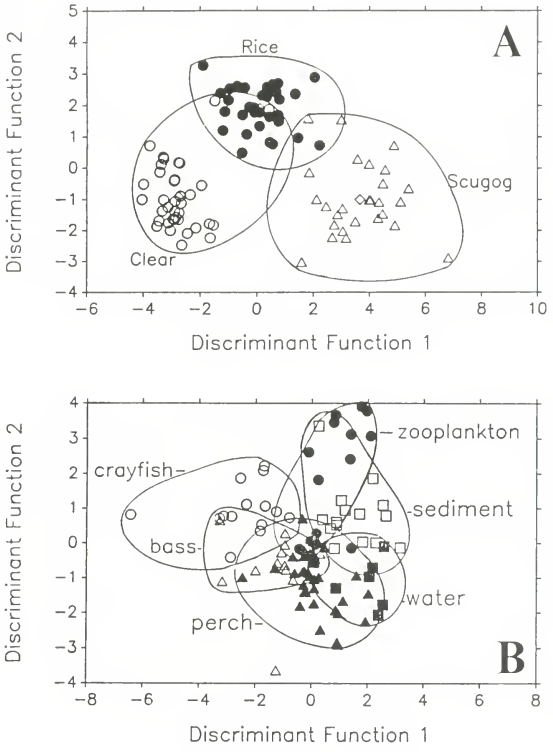


Figure 3 - Whole body PCB concentration data for yearling perch. Solid symbols are from the Ontario Ministry of the Environment (unpublished data) and broken symbols are calculated from total congener data from this study (see text).

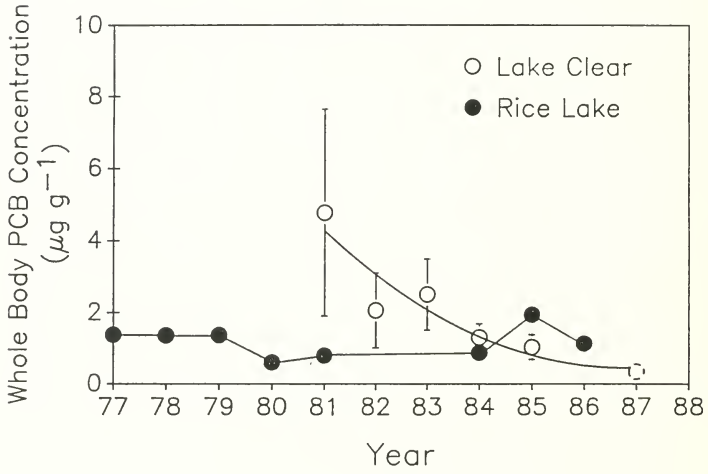
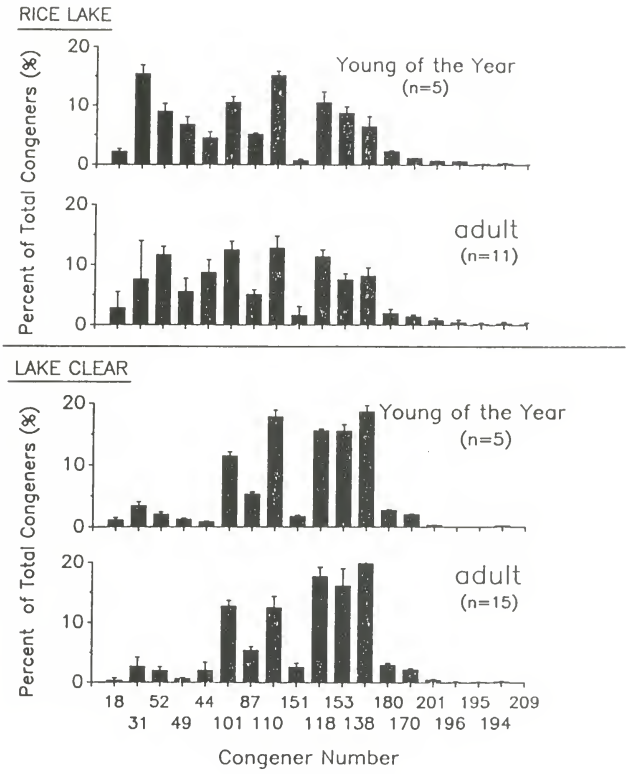


Figure 4 - Comparison of congener patterns in yearling and adult perch in Rice Lake and Lake Clear. Numbers in brackets are sample sizes.



Temporal Trends and Distribution of PCBs in Lake Clear; A Small, Contaminated Lake in Ontario

C.D. Metcalfe and C.R. Macdonald

ABSTRACT

Lake Clear, a small, isolated lake in eastern Ontario, Canada, was contaminated with polychlorinated biphenyls in the mid to late 1970's. Samples of biota collected in 1986 and 1987 show that PCB levels in the biota have declined markedly since the early 1980's. The consistency of the pattern of PCB congeners in sediment profiles, and throughout all classes of biota indicates that there has been little "weathering" of PCBs with time. Trends in the distribution of individual PCB congeners throughout the lake ecosystem were tested statistically using two methods. It was determined that the proportion of lower chlorinated congeners was significantly higher in the water and suspended solid phases than in sediments and biota. Principal component analysis indicated that sediment PCBs differed little from the Aroclor 1254 which originally contaminated the lake. The pattern of PCB congeners in biota were the same for all species; including short-lived organisms (e.g. zooplankton, YOY perch) and fish species greater than 10 years of age (e.g. whitefish, lake trout). All of these analyses indicate that, while the PCBs available for uptake by biota are declining with time in the lake, the various congeners are being lost from circulation at equal rates. It is suggested that Lake Clear may be a simple model for predicting the fate of PCBs in large contaminated lake systems, such as the Great Lakes.

INTRODUCTION

The production of polychlorinated biphenyls (PCBs) in North America reached a peak in the late 1960's, but recognition of widespread environmental contamination by these compounds led to reduced production throughout the 1970's and a total ban on production in 1979. The level of PCB residues in some aquatic environments appears to be declining gradually (Brown et al.

1985, DeVault 1985, Suns et al. 1985), but in other areas, PCB residues have remained constant (Norstrom et al. 1988, Addison et al. 1984, Schmitt et al. 1985). It has been suggested that the decline in PCB residues in some aquatic systems may be attributed primarily to "weathering"; that is, a decline in the proportion of less chlorinated PCB congeners (Brown et al. 1985). Thus, higher chlorinated PCBs, which include the most toxic congeners (Kannan et al. 1988), may remain at constant levels in the aquatic environment because they are less volatile, more soluble in lipids, adsorb readily to sediments, and are more resistant to metabolic and microbial degradation (Kenaga and Goring 1980, Shiu and Mackay 1986, Murphy et al 1987, Sawhney 1987, Connell et al 1988).

Both sedimentation and volatilization are important physical mechanisms for removal of PCBs from aquatic systems. Swackhamer and Armstrong (1986) suggested that volatilization was as important a mechanism as sedimentation in the removal of PCBs from Lake Michigan. In a small, remote lake, volatilization was more important than sedimentation in removing PCBs from the water-column (Swackhamer et al 1988). In this latter study, losses through volatilization and sedimentation were greatest for less chlorinated congeners. Theoretical modelling of the partitioning of PCBs between water, particulates, and the atmosphere (Burkhard et al 1985b) indicate that PCB mixtures may or may not weather with time, depending upon environmental conditions. Recent studies on microbial decomposition of PCBs in aquatic sediments (Brown et al 1987, Quensen et al 1988) indicate that there can be dechlorination and eventual aerobic degradation of PCBs in highly contaminated sediments. Less chlorinated congeners substituted at the meta and para positions are most susceptable to dechlorination.

Very few studies have been done to document variations in the congener composition of PCBs in the various species and trophic levels of contaminated lakes. Oliver and Niimi (1988) showed that in Lake Ontario biota, there was a great difference in congener composition between the water phase and plankton, but in higher trophic levels the congener composition remained constant. It is expected that any weathering of PCBs would first become evident among the biotic community in short-lived organisms that accumulate PCBs directly by absorption from the aqueous phase (e.g. zooplankton).

It is difficult to test hypotheses regarding the decline in PCB residues using field data gathered from large aquatic

ecosystems, primarily because of the large number of factors that influence the distribution of individual congeners. These interferences include rates of water replacement, continuing inputs from point sources and the atmosphere, sediment resuspension and mixing within the lake, and, in the case of biota, a range of factors including diet, age, and migratory behaviour of individual species. In addition, large contaminated lakes often have a history of multiple inpoint sources involving a number of different commercial PCB mixtures (i.e. Aroclors 1242, 1248, 1254, 1260). These problems of data interpretation are evident in Lake Ontario, where PCB residues in fish continue to decline in some areas, but have recently begun to increase in other areas (Suns et al. 1983, Suns et al. 1985).

It is the purpose of this study to document historical trends in the decline of PCBs and to characterize the recent distribution of 19 PCB congeners in the biota, water, and sediments of Lake Clear, Ontario, Canada; a small freshwater lake contaminated with PCBs in the mid-1970's. We wish to determine whether the distribution of PCBs in the biota and sediments of contaminated lake systems are modified with time according to the physical properties and structure of the congeners. From the literature, it is expected that PCB residues will reach the highest concentrations in biota with the highest lipid levels, and these residues will decline slowly with time as older individuals are replaced by younger. For the individual PCB congeners, it is predicted that there will a relatively low proportion of less chlorinated congeners throughout the lake because of physical processes (sedimentation, volatilization) and microbial degradation. This "weathered" composition of the PCBs will be particularily evident in short-lived organisms within lower trophic levels. Using historical data, we will estimate the rate at which biota in the lake are recovering from the very high PCB concentrations reported in the late 1970s and early 1980s.

METHODS AND MATERIALS

Study Area and Historical Data

Lake Clear is a small, moderately eutrophic lake in the eastern part of Ontario, Canada (Fig. 1), with a surface area of 1730 hectares and a mean depth of 11.2 m (maximum = 42.7 m). A thermocline is established in June-July and oxygen levels in the

hypolimnion may drop to 1-10% of saturation; probably because of eutrophication caused by cottages on the lake and the presence of a tourist industry since the 1930's.

Historical data on sport fish indicate that by 1978 the lake had become contaminated with a significant quantity of PCB's; probably Arochlor 1254. Contamination originated at the western edge of the lake (Fig. 1), where PCB-laden oil was used on the road to suppress dust. In 1983, the contaminated road surface was removed to a containment facility. It has been estimated (OME, unpublished report), that the period between contamination and removal of the road surface was 7 to 8 years.

Historical data from 1978 to 1985 on concentrations of PCBs in Lake Clear fish and sediments were obtained from the OME. These unpublished data were generated from the ministry's Ontario-wide monitoring program for sport fish, and from several specific OME projects on Lake Clear during 1981 to 1985. Fish were analyzed for total PCB residue levels on a wet weight basis and sediments were analyzed for total PCBs on a dry weight basis (ng g-1) by packed column gas chromatography (LRGC-ECD). Dorsal muscle tissues were analyzed for all fish, with the exception of YOY yellow perch, where PCBs were analyzed from whole fish samples.

Sample collection

Biota and sediments were collected in October 1986 and June 1987 in the areas shown in Figure 1. Crayfish (Procambarus sp.), clams (Elliptio complanata), and "mixed invertebrates" (mainly trichopteran, ephemeropteran, and odonate insect larvae) were collected using hand-held dip-nets. Zooplankton were collected using a 0.25 m^2 conical net made of canvas, 276 um nytex mesh and brass cod bucket. Tows were made for approximately 5 minutes at a depth of 5 m and the plankton collected in 2-3 tows grouped to give one sample. The plankton were further concentrated by passing the sample through 64 μm mesh.

Golden shiner (Notemigonus crysoleucas) and adult and young-of-the-year (YOY) yellow perch (Perca flavescens) were collected in water of 0.5 to 1.5 m depth using a 20 m bag seine. White sucker (Catostomus commersoni), large adult perch and a single lake trout (Salvelinus namaycush) were collected in 1.3 or 2.6 m trap nets in October 1986. Except for the trap nets, all sampling equipment was soaked in reagent grade methanol prior to sampling. Whitefish (Coregonus clupeaformis) and smallmouth bass

(Micropterus dolomieui) were collected by the Ontario Ministry of Natural Resources in Pembroke, Ontario. Total body weight and length of all fish were measured in the field prior to dissection and freezing. Samples of muscle tissue were collected for residue analysis for all fish species, and for crayfish. A sample of muscle tissue was taken from the dorsal area of the fillet below the dorsal fin for lake trout, bass, whitefish, white sucker, and adult yellow perch samples. With smaller fish (golden shiner, YOY perch), the head, tail, and internal organs were removed before analysis. Crayfish samples consisted of muscle dissected from the tail, and clam samples consisted of soft tissue removed from the valves. Since only one lake trout was collected, 4 subsamples of dorsal fillet were prepared for residue analysis of this fish.

Sediment cores were collected at a depth of approximately 30 m using a K-B corer with brass tubes 0.35 m in length. After collection of the core, a plug was inserted into the bottom of the brass tube and the core elevated in increments of 3 cm. The individual 3 cm sections were collected in an aluminum sectioning device which was cleaned between samples. The sections were stored separately in clean, solvent washed 250 ml Mason jars. Sediments for analysis of total organic carbon were collected by Ekman grab.

Water samples were collected by hand-pumping water with a stainless-steel and teflon solvent pump from a depth of approximately 1 m into a stainless steel container. Volumes of 18 L of lake water were passed through 137 mm diameter organic binder-free filters (pore size of 0.3 μm) into a 20 L stainless steel extraction vessel. Two volumes (500 and 400 ml) of distilled-in-glass methylene chloride were added to the water in the extraction vessel, each stirred for 15-20 min, and removed into a 1 L amber glass bottle by displacement with nitrogen gas. Particulates on the 0.3 μm filters were stored in solvent washed 250 ml Mason jars with approximately 100 ml of methylene chloride. "Grab" samples of water were collected by pump for analysis of pH, alkalinity, suspended solids, and DOC.

All sediment, suspended sediment, and biota samples were stored in 250 or 500 ml Mason jars, which had been washed with reagent grade acetone and pesticide grade hexane and sealed with solvent-washed aluminum foil. All biota samples were frozen within 8 hours of collection and remained frozen until analysis.

Sample Preparation

Sediment samples of approximately 5 g were prepared for analysis according to method "A" of the Ontario Ministry of the Environment protocol for analysis of organochlorine pesicides and PCBs in sediments (OME, 1983). Briefly, sediments were extracted with acetone by sonication, and back-extracted into methylene chloride. The extract was dried by passing through sodium sulfate and rotary evaporated to 2 ml for sample cleanup and fractionation. Samples were cleaned up and fractionated into three subfractions by column chromatography (1 cm i.d.) on 5 g of activated silica gel (60-200 mesh). The column was eluted with 40 ml of hexane to yield Fraction A (PCBs, DDE, aldrin, lindane, heptachlor, and mirex), and the column was subsequently eluted with 40 ml of 25% methylene chloride in hexane, and 40 ml of 40% methylene chloride in hexane to yield organochlorine pesticide subfractions B and C, respectively. Sulfur compounds were removed from Fraction A by precipitation with mercury.

Biota samples of approximately 5 g were ground with sodium sulfate in a mortar, and extracted into hexane with a soxhlet apparatus for 1 hr. A subsample of the extract was rotary evaporated to 2 ml and made up to 5 ml in 55:45 hexane:methylene chloride. Lipids were removed from this extract by gel permeation chromatography on a 3 cm i.d. X 28 cm column of Biobeads SX2 (200-400 mesh). The column was eluted at a rate of 2 ml per minute with 55:45 hexane:methylene chloride. The first 90 ml of eluent, which contained lipid, was collected and evaporated to dryness for gravimetric determination of lipid content. The next 100 ml of eluent, which contained PCBs and organochlorine pesticides, was collected and subjected to further cleanup before analysis. The extract was cleaned up and fractionated by silica gel column chromatography, as described for the sediment extracts.

The methylene chloride collected in the field from two water samples (2 x 18 L) was passed through sodium sulfate, pooled, and rotary evaporated to 2 ml. The extract was partitioned into hexane by successive additions of hexane and evaporation under nitrogen. The sample was then cleaned up and fractionated by silica gel chromatography, as described above. The glass fibre filters containing suspended particulate material from two water samples (2 x 18 L) were pooled and manually broken up while immersed in the methylene chloride originally added in the field. The entire sample was filtered under vacuum through sodium

sulfate in a Buchner funnel. A further 150 ml of methylene chloride was then passed through the filter. The extract was partitioned into hexane and cleaned up/fractionated by silica gel chromatography, as described previously.

Sample Analysis

Sediment samples were analyzed for organic carbon content and particle size distribution, and water samples were analyzed for pH, alkalinity, suspended solids, and DOC according to Ontario Ministry of the Environment protocols (OME, 1983).

Samples were analyzed for PCBs by high resolution gas chromatography (HRGC-ECD) on a Varian 3500 gas chromatograph, using a 30 m DB5 capillary column (250 um OD, 25 um ID) and splitless injection. The flow of hydrogen carrier gas was 1.8 ml/min and the flow of nitrogen make-up gas into the EC detector was 28 ml/min. GC conditions were: injector 250°C, detector 275°C, and initial column temperature 80°C. The column temperature was programmed as follows: 1 minute hold time at 80°C, increase at 4°/min to 160°C, increase at 1.5°/min to 230°C, increase at 7°/min to a final temperature of 250°C, with a final hold time of 20 min. Individual congeners were identified by retention time (window 0.02 %), and quantified from integrated peak areas. Detection limits for individual congeners varied from 0.02 to 0.05 ng/ml.

Quantification of individual PCB congeners was made by comparison to standards purchased from the National Research Council in Halifax, Canada. The standard was a mixture of the NRC standards CLB-1 A and D, to which congener 52 (2,2',5,5') was added. DDE was added as a relative retention time marker. Nineteen congeners were chosen for analysis (Table 2), the sum of which represented 46%, 53%, and 62% of the total PCBs present in Aroclors 1242, 1254, and 1260, respectively.

Of the 19 congeners quantified from the standard, 4 of the congeners coeluted with other PCB congeners present in environmental samples (Table 2). All coeluting peaks were reported as the concentration of the congener present in the standard, with the exception of congener 77 which coeluted with congener 110. Since congener 77 (3,3',4,4') makes up a very small proportion of PCBs in commercial Aroclors in comparison to congener 110 (2,3,3',4',6), it was assumed that no congener 77 was present in the Lake Clear samples. Since there are no purified standards of congener 110 available, congener 77 in the standard was used as a

retention time marker for 110 and was used to calculate concentrations of 110 in Lake Clear samples. The integrated area of the peak eluting at the retention time for 77 was multiplied by the response factor for congener 77 times the ratio of the relative response factors for congeners 77 and 110, as determined by Mullin et al (1984).

Data Treatment and Statistical Analysis

PCB levels determined by HRGC-ECD are reported either as the total of the 19 congeners analyzed, or as the relative proportion of individual congeners to the total. The bioconcentration factor (BCF) for each congener was calculated as the ratio of the concentration of each congener in biota to the concentration in water.

Total congener concentrations in biota were calculated both on a wet weight basis and a lipid weight basis. Lipid levels in the 4 to 5 g samples were often close to detection limits for gravimetric analysis. Hence, for 1 clam and 1 whitefish sample the lipid value was estimated from the mean of the other 4 samples.

To relate historical PCB residue data to more recent data, it was assumed that the sum of the 19 PCB congeners analyzed by HRGC-ECD represented 50% of the total PCB's analyzed by LRGC-ECD. Thus, estimates of total PCB residues were made by doubling the total congener concentrations. Where necessary, whole-body concentrations of PCBs in fish were estimated by multiplying muscle concentrations by a factor of 2.5 (Niimi and Oliver 1983).

All data were analysed using the personal computer version of SPSS software (SPSS/PC, Inc., Chicago, Ill. 1988). Significant differences were measured at the 0.05 level (i.e. $P<0.05$). All means and range tests were calculated using log transformed data to normalize the residuals.

Principal component analysis was conducted using SPSS/PC and EINSIGHT (Infometrix, Inc., Seattle, Washington), which use methods of calculation common to chemometrics (Sharaf et al., 1986). The congener composition data for each sample were entered in a single matrix and rotated using a varimax rotation (SPSS-PC 1988). Random numbers between 0 and the detection limit were entered for all data in which congener residues were undetectable. Congener 209 (decachlorobiphenyl) was removed from the principal component analysis because it was rarely detected in Lake Clear samples.

RESULTS

Historical Monitoring Data

By 1978, total PCB concentrations in the dorsal muscle of lake trout and northern pike in Lake Clear were greater than 2,000 ng g^{-1} wet weight. PCB residues from lake trout collected in 1980, 1981, and 1982 ranged widely from 660 ng g^{-1} to 15,800 ng g^{-1}. Whitefish, smallmouth bass, adult yellow perch, and common white suckers were also heavily contaminated with PCBs (Table 2). A survey of whole-body PCB residues in yearling yellow perch collected during 1981-1985 from the western portion of the lake indicates that there was a decline in mean total PCB concentrations from a maximum of 4770 ng g^{-1} in 1981 to 907 ng g^{-1} in 1985.

Samples of the contaminated road surface and adjacent lake sediments collected in 1981 and 1982 revealed very high concentrations of total PCBs. The road surface contained up to 300 μg g^{-1} PCBs, and lake sediments 15-30 m offshore contained from 1 to 10 μg g^{-1} of total PCBs. In 1982, PCB concentrations in surface sediments from the deepest area of the lake (see area marked "sed" in Fig. 1) were 0.45 μg g^{-1} dry weight.

Recent Monitoring Data

a) Water, Suspended Solids, and Sediments

Water samples collected in 1987 had a DOC concentration of 2.83 mg L^{-1} (SD = 0.05, n=6), alkalinity of 111.2 mg L^{-1} (SD=0.34, n=6) and pH of 8.4. Suspended solids, which were composed primarily of detritus and phytoplankton, were at a concentration of 1.08 mg L^{-1} (SD=0.78, n=10). The concentration of total PCB congeners dissolved in water was 1.95 ng L^{-1}(n=2), and the concentration on suspended solids was 897 ng g^{-1} dry weight (n=2).

Size distribution analysis of the sediments indicated that 65% (SD=5.1, n=5) of the particles were less than 45 μm, with the remaining 35% in the range of 45 - 1000 μm. As indicated in Table 3 for samples collected in 1987, the mean concentration of total PCB congeners in the surface sediment (0-3 cm) was 597 ng g^{-1} dry weight, but the concentration decreased with depth. Total organic carbon content of the sediment was 11.2% (SD=13.0, n=5), giving a concentration of 5.35 μg g^{-1} C in the 0-3 cm section (Table 3).

b) Biota

For biota samples collected in 1986-87, the geometric means and standard deviations for total body weight, total length, lipid content, and total congener concentrations on both a wet weight and lipid weight basis are summarized in Table 3. Mean ages of mature fish ranged from approximately 4 years in smallmouth bass and adult perch (as determined by scale reading), to approximately 12 years in the single lake trout (as estimated from Hoyle and Stewart, 1987). Yellow perch spanned a range of ages from 0^+ to 7^+, with the "intermediate" sized fish estimated to be approximately 1^+ and 2^+ years. Ages of the white suckers and whitefish were estimated from body length to be approximately 10 years and 4 years respectively, based on data from similar lakes (Scott and Crossman 1973).

Lipid values ranged from a minimum of 0.15% in the whole body sample of the clams to 11.3% in the muscle tissue of golden shiner. Golden shiners, the single lake trout, and zooplankton contained the highest levels of lipid. There was no correlation between the lipid content of the biota and total PCB concentrations on a wet weight basis ($P > 0.05$). Total PCBs (wet weight) ranged from 23.6 ng g^{-1} in the clam sample to 2993 ng g^{-1} in the lake trout. However, the majority of biota samples were in the range of 60-150 ng g^{-1}. Excluding the lake trout sample, the highest wet weight PCB residue levels were in smallmouth bass, white suckers, and whitefish. Scheffe's multiple range test grouped these species with YOY perch and golden shiner as having significantly greater PCB concentrations than clams, crayfish and zooplankton.

There were some shifts in the relative concentrations of total congeners in biota when expressed on a lipid weight basis (Table 3). Maximum PCB concentrations were observed in lake trout, crayfish, and older perch (>1 y). Smallmouth bass and white sucker, which contained among the highest residue concentrations on a wet weight basis, were in the middle of the range on a lipid basis.

Yellow perch was the only species for which sufficient samples were analyzed to permit statistical tests of relationships between PCB levels and age. There was no significant relationship between PCB concentration and age on either a wet weight or lipid weight basis, even though muscle lipid levels decreased significantly with age ($P<0.001$, $r^2=0.53$). As another approach, whole body concentrations of total congeners were estimated as 2.5 times the muscle concentration, and whole

body burdens calculated as [body concentration x body weight]. There was a linear relationship between age and the log of total body burden in yellow perch ($P<0.0001$, $r^2 = 0.88$), with a slope of 0.306.

Congener Distributions

The concentration of the individual congeners in sediments, water, suspended solids, and biota are shown in Figure 2 as a proportion of the total PCB congeners. The major congeners in all biota samples, including zooplankton, are the pentachlorobiphenyl compounds 101, 110 and 118 and the hexachlorobiphenyl congeners 149 (co-eluting with congener 118), 153 and 138; the same congeners that are dominant in Aroclor 1254 (Fig. 2). These same congeners are prevalent in all 3 sections of the sediment core, although only the data for surface sediment are shown in Figure 2. The congener patterns in water and suspended solids were different from all biota and sediment samples, and showed a higher proportion of lower chlorinated congeners.

Shifts in the proportion of individual congeners analyzed in biota, sediment, water, and suspended sediments were examined statistically using two methods. The first method consisted of analyzing the proportions of 5 structurally related congeners (congeners 18, 52, 101, 180 and 194) in water, sediment, and biota, using analysis of variance and range tests to determine significant differences between groups (Fig. 3). This analysis, which is similar to that of Oliver and Niimi (1988), indicates that the proportion of a tri- (18) and tetrachlorobiphenyl (52) to total congeners was significantly higher in water, suspended solids, and invertebrate biota, while the proportion of a hexachlorobiphenyl (153) was elevated in biota from upper trophic levels. The most highly chlorinated PCB congener detected (194) remained at a constant proportion throughout all compartments (Fig. 3).

In the second type of analysis, principal component procedures were used to illustrate the degree of similarity or dissimilarity in congener patterns among the different compartments of the Lake Clear ecosystem. Standards of Aroclors 1242, 1248, 1254 and 1260 were included in the analysis as reference points and to indicate the sensitivity of the analysis to changes in the distribution of congeners. Principal component analysis of all sediment, water, suspended solids, biota, and the standards reduced the data to 3 factors which accounted for 81%

of the total variability (Table 4). The first principal component consisted of all of the hepta- and octachlorobiphenyls (congeners 196, 201, 180, 170, 194, 195) plus the hexachlorobiphenyl congener 151, and separated Aroclor 1260 from all other groups (Fig 4; Table 4). There was no similarity between any of the samples and Aroclor 1260 (Fig 4). The second principal component, which consisted of tetrachloro- and hexachlorobiphenyls (congeners 52, 44, 153, 49 and 138) produced the greatest separation between samples and Aroclor mixtures (Fig. 4), and was responsible for 35% of the total variation. When the data were reanalysed without Aroclor 1260, the second component became dominant, accounting for 53% of the variability. The third component of the full analysis explained 7.2% of the variability and consisted of tri- and pentachlorobiphenyls.

Separation of the Lake Clear samples was most evident along the second principal component (tetra- and hexachlorobiphenyls), with the water samples showing a distinct similarity with Aroclors 1248 and 1254. Suspended solids samples were variable, and were not aligned with any Aroclor mixture with respect to the second component. These groupings reflect the higher proportion of less chlorinated congeners in water and suspended solids. All surface sediment samples showed a strong correlation with Aroclor 1254 in all 3 principal components, indicating that the pattern of congeners in sediment was similar to this Aroclor product. In general, all biota responded to the principal components analysis as a group. There was no consistent differentiation of any particular species or trophic level. Hence, in Figure 4, all biota are represented by a single symbol. The biota were most closely associated with Aroclor 1248 along the third component (tri- and pentachlorobiphenyls).

DISCUSSION

The historical data indicate that a significant quantity of PCBs, probably Aroclor 1254, entered Lake Clear in the mid to late 1970's, although the exact time of contamination is difficult to determine. Data from 1986-87 indicate that contamination is still present in all groups of biota, water and sediment, although the concentrations are generally lower than in the early 1980's. For example, PCB levels in whitefish and smallmouth bass decreased from mean values of 5134 and 1194

ng g^{-1} in 1982 to approximately 208 and 306 ng g^{-1}, respectively, in 1987; assuming that the 19 congeners analysed in the present study account for 50% of total PCBs. PCB concentrations in lake trout appear to have remained relatively constant from 1980 to 1987 (approx. 6,000 ng g-1), although data interpretation is hampered by the extreme variability in concentration between fish, and the small sample size in 1987 (n=1).

A decrease in total PCB concentrations is most evident in yearling to YOY yellow perch samples, where concentrations declined from a maximum mean of 4770 ng g^{-1} in 1981 to 907 ng g^{-1} in 1985. When total congener data for muscle tissue is converted to whole-body total PCBs, the levels in YOY perch in 1987 are equivalent to approximately 350 ng g^{-1}; consistent with a continuing decline in PCB levels (Fig. 5). An exponential decay relationship fitted to the perch data (Fig. 6) corresponds to a half-life of 1.73 years.

Declining PCB concentrations in biota suggest that the amount of PCB available to the biota is decreasing at a significant rate. Possible major routes of loss of PCBs include volatilization (Swackhamer et al. 1988), microbial degradation (Brown et al. 1987, Quensen et al 1988) and adsorption onto particulates followed by sedimentation (Thomann, Connally and Thomas, 1987).

Although Henry's Law Constants for individual PCB congeners cover a broad range of values (Burkhard et al. 1985a, Shiu and Mackay 1986, Murphy et al. 1987, Dunnivant et al. 1988), volatilization of PCBs has been suggested as a major mechanism for the removal of PCBs from lake systems; especially among less chlorinated PCB congeners. Swackhamer et al. (1988) constructed a mass balance for an isolated lake which showed that the losses of PCB'ś to the atmosphere were equal to the losses by sedimentation, and that the highest volatilization losses were for congeners 18 (trichlorobiphenyl), 52 and 49 (tetrachlorobiphenyls), and 101 (pentachlorobiphenyl). In the present study, it would be expected that these congeners, plus congeners 31(28) and 44, would be most susceptible to losses through volatilization.

Similarly, microbial degradation of lower chlorinated PCB congeners does occur in sediments (Brown et al. 1987, Quensen et al. 1988), although the extent of the process is unclear (Brown et al. 1988) and appears to only occur at very high concentrations of PCB. Although primarily trichlorobiphenyls and tetrachlorobiphenyls are degraded in pure culture (Furukawa et

al. 1978), in natural sediments, the position of chlorines on the biphenyl ring can be a strong determinant of degradability. Brown et al. (1987) reported microbial dechlorination of congeners 18, 52, 49, 110 and 118.

The distribution of major PCB congeners in the samples collected in 1986 and 1987 indicate that losses due to either volatilization or microbial degradation are undetectable at this point. The presence of less chlorinated congeners in the water phase suggests that there is still a large pool of tri- and tetrachlorobiphenyls in the lake. Using the values of Swackhamer et al. (1988) as conservative estimates of the quantity of congeners lost to the atmosphere from a small northern lake (710 ng m^{-2} y^{-1}), then approximately 12 g per year of congener 18 would volatilize from Lake Clear, and about half that amount of congeners 101 and 52 would be lost. Assuming that the replacement of these congeners through atmospheric sources is low compared to the original input, we would have expected a skewing of congener distribution towards more highly chlorinated compounds (Burkhard et al 1985b), had volatilization been a major fate process.

The same argument applies for the possible losses of PCBś through microbial degradation. The lower chlorinated congeners, such as 52 and 49, which appear to be particularly susceptible to dechlorination in sediments (Brown et al. 1987), remain at a relatively constant proportion of the total congeners at all depths in the sediment core. Principal component analysis grouped the surface sediment samples with Aroclor 1254; indicating a strong similarity between the PCBs in sediment and the Monsanto product thought to have been applied over 10 years ago to the road near Lake Clear.

Further evidence for the lack of weathering of the PCB's can be seen in the congener distribution within tissues of short-lived organisms, such as zooplankton and YOY perch, which have been exposed to Lake Clear contamination for only a matter of months. The samples are generally lower in total congener concentration than the higher trophic levels, but demonstrate the same congener patterns as fish which have been in the lake for 10-12 years (whitefish and the lake trout).

PCBs are being removed from general circulation within the lake, but this is obviously occurring at a relatively constant rate among all PCB congeners. This is most likely to occur by partitioning into sediments. Sedimentation of PCB's in Lake Clear is obviously an on-going process since, in 1987, the

highest total congener concentrations in the sediment were 597 ng g^{-1} in the top 3 cm (corresponds to 1194 ng g-1 total PCB), and the pattern of congeners was constant from the surface to 9 cm. In 1982, total PCB concentrations in the surface sediments at this same site were 450 ng g^{-1}. In 1987, total congener concentrations in the sedimenting material (suspended solids) were higher (897 ng g^{-1}) than in the surface sediment.

Using simulations based on fugacity models, Burkhard et al (1985) predicted that there will be little weathering of PCBs in aquatic systems, unless the various compartments within the system experience multiple equilibrations. A model based on the latter scenario which simulated the continuous movement of "clean" air across PCB-contaminated water indicated that less chlorinated congeners (i.e. highest Henry's law constants) would be preferentially removed; resulting in an enrichment of more highly chlorinated congeners with time in all compartments of the system. In "sedimentation" simulations, the continuous renewal of "clean" suspended particulate material to the system resulted in an initial enrichment of more highly chlorinated congeners (i.e. highest Kp values) in bottom sediments, but this trend decreased with time. There is no evidence that either of these processes are active in Lake Clear. Since enrichment of highly chlorinated congeners has been noted in the Hudson River sediments (Brown et al 1985), the lack of weathering noted in Lake Clear may be a specific characteristic of contaminated lake ecosystems.

The temporal trends in PCB residue concentrations within biota have implications to the sport fish industry. Within Lake Clear biota, there appeared to be no differences in PCB concentration between pelagic and benthic organisms, or between trophic levels. Surprisingly, the highest concentrations on a lipid weight basis were observed in crayfish muscle. There was no significant difference between PCB residues on a lipid weight basis in top predators (smallmouth bass, lake trout) vs. omnivorous fish (white sucker, perch).

The single factor which does appear to influence PCB concentration is time of exposure, as indicated by the age of the organism. Although it is not statistically significant, PCB concentrations (lipid basis) in younger organisms (YOY perch, zooplankton) contain low PCB concentrations relative to lake trout, smallmouth bass whitefish, and white sucker. These observations are consistent with the conclusions of Weininger (1978) who concluded that the concentration of PCBs in lake trout in Lake Michigan are better described as a function of the age of

the fish than the amount of lipid or the partition coefficient of the PCB mixture.

Accumulation of PCBs with age was observed in yellow perch from Lake Clear. Regressions relating perch age to total body weight and estimated body burden of PCB's give the equations:

log (body weight, g) = 0.582 + 0.322 age(y) $r^2 = 0.88$

log (body burden, μg) = -0.076 + 0.306 age (y) $r^2 = 0.85$

Hence, between the first and second year, both the body weight and body burden of PCBs in perch increase by a factor of approximately 2. If it assumed that the fish feed on a diet of zooplankton with a PCB concentration of 60 ng g^{-1}, at a feeding rate of 2% body weight per day, with a PCB uptake efficiency of 60% (Thomann et al. 1987), then the fish will accumulate approximately 2.5 $\mu g\ y^{-1}$ from its diet alone; close to the observed value. Once PCBs are accumulated in fish, there is no evidence that any of these residues will be lost with time. Thus, the declines in PCB concentrations noted in sport fish within Lake Clear are presumeably taking place as older, more contaminated fish disappear from the population.

The distribution of individual PCB congeners in biota followed expected patterns, in that the proportions of higher chlorinated congeners were statistically higher in biota than in water and suspended solids. The proportion of some of the congeners increased significantly through the food web (e.g. congener 153), but, in general, the congener patterns in all biota samples were remarkably consistant. Oliver and Niimi (1988) observed that the greatest difference in congener composition throughout the lake Ontario food web was between plankton and the water phase. Similarily, in Lake Clear, there is a marked difference in dominant congeners between zooplankton and water, but a strong similarity within biota as a whole. This is shown in the distinct grouping of biota in the principal components analysis. Hence, the enrichment of moderately chlorinated congeners by biota is the same for both "young" and "old" individuals, and does not reflect weathering of PCBs with time.

An examination of temporal changes and distribution of PCBs in Lake Clear shows that residue levels in biota have declined measurably within approximately 10 years post-contamination. In contrast, within sediments in a deposition zone of the lake, PCB concentrations appear to have increased in recent years. The stable pattern of congeners in sediments and within biota of all ages suggests that PCB weathering has not occurred with time. These data indicate that volatilization is not a major route for

loss of less chlorinated PCB congeners from contaminated lakes. These characteristics may be specific for contaminated lakes, as opposed to contaminated rivers or lakes receiving atmospheric deposition. If this is the case, Lake Clear may be a relatively simple model for predicting the fate of PCBs in larger contaminated lakes, such as Lake Ontario, Lake Michigan, and Lake Erie.

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Table 1 - Historic PCB levels in Lake Clear fish (Ontario Ministry of the Environment)

Species	n	Mean Weight (g)	Mean Length (cm)	% Lipid	PCB Concentration (ng g^{-1})
1978					
lake trout	1	1092	48.3	2.7	2530
northern pike	4	1316 (756-1960)	60.3 (50.8-71.0)	0.5	2197 (1300-3700)
1980					
lake trout	5	2710 (2520-2912)	65.0 (62.4-67.2)	3.8	6319 (3564-9081)
northern pike	16	1275 (252-4088)	56.1 (37.1-83.0)	0.4	353 (108-951)
1981					
lake trout	18	3147 (2000-5500)	65.2 (56.0-75.0)	5.5	8253 (3092-15800)
northern pike	20	1199 (500-2000)	56.5 (38.7-68.0)	0.1	406 (43-1623)
smallmouth bass	1	300	28.0	1.0	727
whitefish	10	923 (425-1600)	42.9 (37.0-49.0)	ND	2194 (326-6392)
yellow perch	15	201 (150-300)	26.3 (24.6-28.2)	ND	321 (188-619)
yellow perch (yearling)	5	NR	6.1 (6.0 - 6.3)	ND	1716 (1524-1968)
1982					
lake trout	12	3582 (1150-6015)	68.6 (49.0-83.5)	6.5	5933 (660-9100)
lake trout	7	3296 (2240-4032)	66.2 (60.5-70.4)	6.1	6293 (1679-9397)
northern pike	36	1255 (364-3248)	57.8 (31.2-82.2)	0.5	606 (128-1997)
common white sucker	20	1308 (364-2128)	46.6 (30.8-56.6)	1.0	1105 (57-6376)
smallmouth bass	11	873 (140-1568)	35.6 (22.5-45.1)	1.0	1194 (463-2258)
burbot	21	1310 (182-4500)	50.4 (29.0-75.6)	0.3	305 (92-958)
whitefish	20	1312 (378-2812)	48.9 (34.4-58.2)	3.6	5134 (559-12300)
yellow perch	20	211 (168-294)	27.6 (25.8-29.6)	0.5	567 (250-1144)
rock bass	20	343 (210-434)	25.2 (21.1-27.2)	0.5	760 (136-3849)

ND - not detectable
ND - not reported

Table 2 - Summary of PCB congener IUPAC numbers, chlorine number and substitution patterns analysed in the Lake Clear samples.

Congener Number[1]	Chlorine Number	log K_{ow}[2]	Chlorine Position
18	3	5.24	2,2',5
31(28)	3(3)	5.67(5.67)	2,4',5 (2,4,4')
52	4	5.84	2,2',5,5'
49	4	5.85	2,2',4,5'
44	4	5.75	2,2',3,5'
101	5	6.38	2,2',4,5,5'
87	5	6.29	2,2',3,4,5'
110(77)	5(4)	6.48(6.36)	2,3,3',4',6 (3,3',4,4')
151	6	6.64	2,2',3,5,5',6
118(149)	5(6)	6.74(6.67)	2,3'4,4',5 (2,2',3,4',5',6)
153(132)	6(6)	6.92(6.58)	2,2',4,4',5,5' (2,2',3,3',4,6')
138	6	6.83	2,2',3,4,4',5'
180	7	7.36	2,2',3,4,4',5,5'
170	7	7.27	2,2',3,3',4,4',5
201	8	7.62	2,2',3,3',4,5,5',6'
196	8	7.65	2,2',3,3',4,4',5,6'
195	8	7.56	2,2',3,3',4,4',5,6
194	8	7.80	2,2',3,3',4,4',5,5'
209	10	8.18	2,2',3,3',4,4',5,5',6,6'

[1] - IUPAC numbering system for PCB congeners.
[2] - Log K_{ow} values from Hawker and Connell (1988).

Table 3 - Mean values (standard deviation) for samples collected in 1986 and 1987 in Lake Clear.

Group	Sample Size (n)	Body Weight (g)	Total Length (cm)	% Lipid	PCB Concentration wet weight (ng g^{-1})	PCB Concentration lipid weight (ug g^{-1})
Benthos						
crayfish	5	20.9[1] (11.2-39.0)	8.04 (6.67-9.69)	0.19 (0.10-0.35)	73.2 (38.0-141)	39.1 (11.8-130)
clams	5	44.7[1] (39.1-51.2)	8.12[2] (7.58-8.70)	0.15[1] (0.06-0.42)	23.6 (15.5-36.0)	14.5 (8.71-24.1)
grouped sample	1	-	-	0.58	34.7	3.0
Zooplankton						
grouped sample	5	-	-	1.17 (1.00-1.38)	59.3 (47.7-73.9)	5.06 (4.51-5.68)
Fish						
golden shiner	5	1.73 (1.27-2.36)	6.18 (5.32-7.19)	11.3 (6.55-19.4)	79.7 (69.9-91.0)	0.71 (0.38-1.33)
perch (>1y)	15	67.7 (22.5-204)	19.0 (13.6-26.6)	0.22 (0.17-0.28)	76.3 (47.7-122)	35.1 (21.3-57.7)
perch (YOY)	5	2.74 (1.94-3.87)	6.89 (6.19-7.67)	0.48 (0.36-0.64)	89.8 (79.3-102)	18.9 (13.0-27.4)
common white sucker	5	955[1] (601-1520)	51.5 (47.1-56.3)	0.49 (0.30-0.81)	121 (63.2-232)	24.5 (18.7-32.2)
smallmouth bass	5	720 (682-760)	35.5 (33.9-37.2)	0.75 (0.59-0.97)	153 (125-186)	20.2 (16.7-24.5)
whitefish	5	627 (453-867)	39.9 (36.9-43.2)	0.39[1] (0.26-0.57)	104 (57.9-188)	26.6 (17.8-39.7)
lake trout	1	2100	76.6	6.80	2993	46.8
Sediment						
0-3 cm (surface)	5	-	-	11.2[3]	571[4] (410-796)	5.35 (4.19-6.82)
3-6 cm	5	-	-	11.2	357 (300-424)	3.19 (2.69-3.79)
6-9 cm	4	-	-	11.2	242 (183-320)	2.16 (1.63-2.86)

[1] - mean values based on sample size of 4
[2] - mean length based on shell length of 3 individuals used for PCB analysis
[3] - total organic carbon
[4] - concentration is ng g^{-1} dry weight

Table 4 - Variable loadings for the 3 principal components shown in Fig. 5.

	Factor 1	Factor 2	Factor 3
	196 (8)	52 (4)	87 (5)
	201 (8)	44 (4)	101 (5)
	180 (7)	153 (6)	110 (5)
	170 (7)	49 (4)	31(28) (3)
	194 (8)	138 (6)	18 (3)
	195 (8)		118(149) (5)
	151 (6)		
Variance	40.9%	34.9%	9.0%

Figure 1 - Map of study area showing sampling sights and the location of Lake Clear in Ontario (inset).

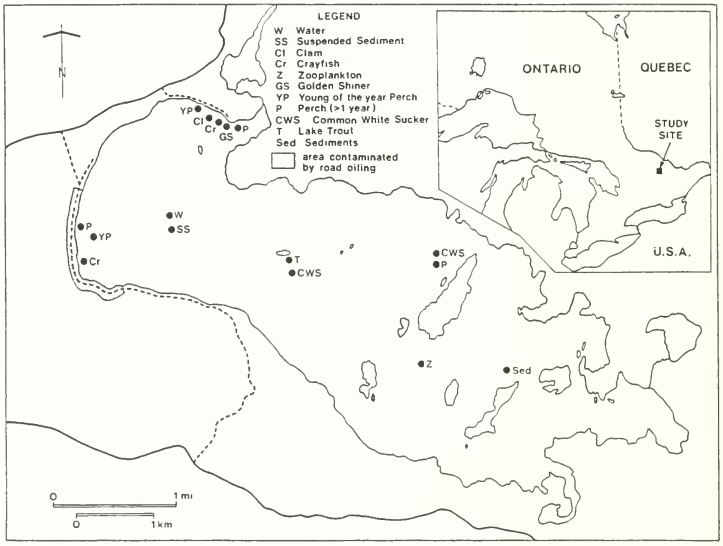


Figure 2 - The proportion of individual congeners in water, suspended solids, surface sediments and 6 groups of biota as a percent of the total congeners. Each bar in the histograms represents a mean value (the number of samples is given in Table 2) with error bars of 1 SD. The histogram for Aroclor 1254 is the mean of 5 determinations.

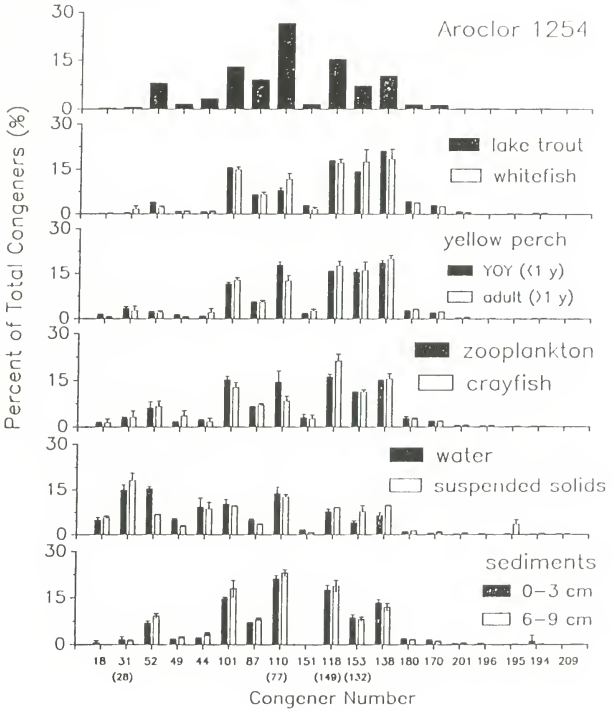


Figure 3 - Comparison of 6 structurally similar congeners in all samples from Lake Clear. See text for statistical comparisons between groups. Legend: WAT - water; SS - suspended solids; SED - surface sediments; ZOO - zooplankton; CL - clams; CR - crayfish; GS - golden shiner; YOP - young-of-the-year yellow perch; ADP - adult yellow perch; CWS - common white sucker; WF whitefish; SMB - smallmouth bass; LT - lake trout.

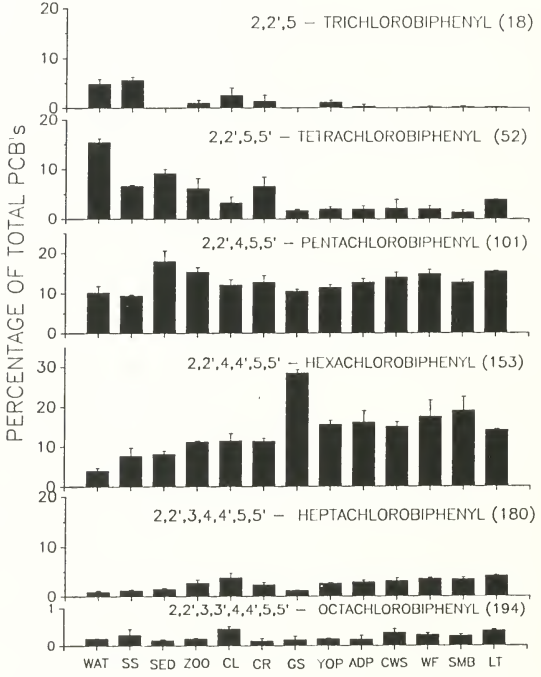


Figure 4 - Principal component analysis of congener proportions in water, suspended solids, surface sediments and biota showing the three major components that account for 82 % of the variability of the data. The numbers on the graphs refer to the means of 5 determinations of Aroclor standards.

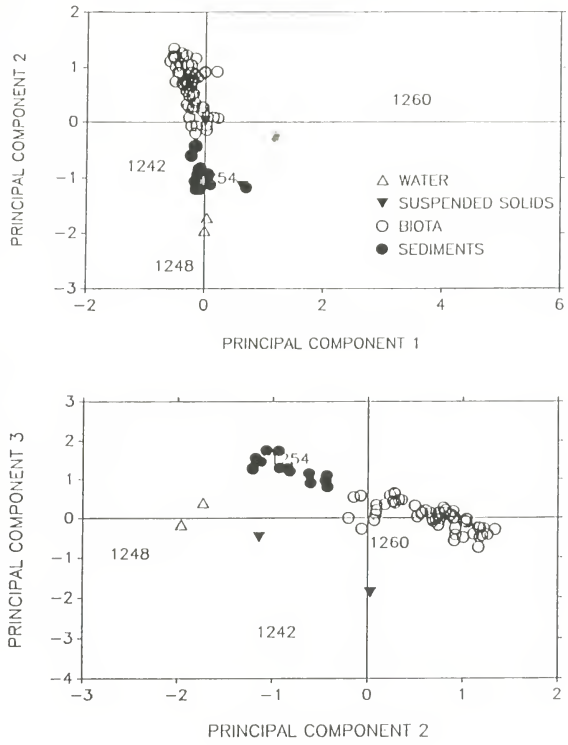
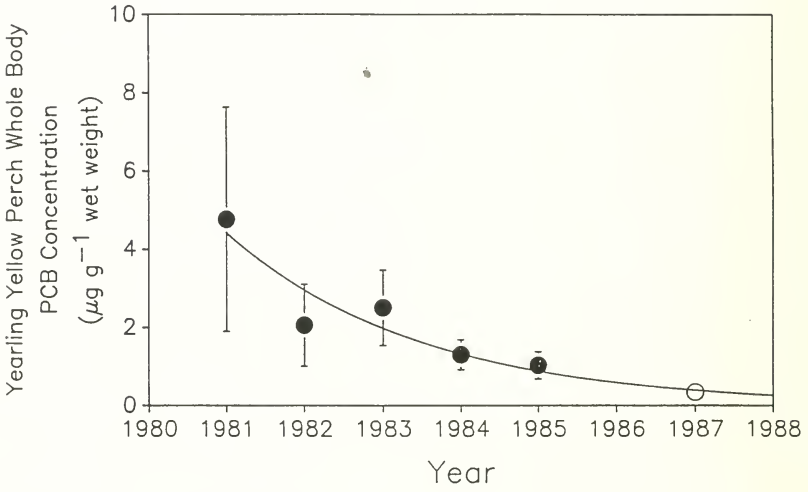


Figure 5 - Decline in the concentration of total PCB in yearling yellow perch whole body. Closed symbols are from the Ontario Ministry of the Environment (unpubl. data) while the open circle is estimated from the congener data of the present study. The solid line is fit with a negative exponential equation (see text).



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AN ECOSYSTEM APPROACH TO THE MONITORING OF PCBs IN PRISTINE LAKES IN ONTARIO

R. A. C. PROJECT NO. 275C

Prepared for Environment Ontario by:

C. D. Metcalfe
Trent University

OCTOBER 1990

Table 3 - Maxi

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ACKNOWLEDGEMENT AND DISCLAIMER

This report was prepared for the Ontario Ministry of the Environment as part of a Ministry funded project. The views and ideas expressed in this report are those of the author and do not necessarily reflect the views and policies of the Ministry of the Environment, nor does mention of trade names or commercial products constitute endorsement or recommendation for use. The Ministry, however, encourages the distribution of information and strongly supports technology transfer and diffusion.

PROJECT OVERVIEW

Environment Ontario programs for the monitoring of contaminant levels in sport fish indicate that moderately elevated levels of PCBs and some organochlorine insecticides are found in fish within inland lakes in central Ontario. These data stimulated speculation on the probable sources of these compounds, and whether contamination of these lakes is an on-going process. The Ministry was particularily interested in determining whether atmospheric deposition of PCBs and other organic contaminants could be a major source of contamination of sport fish.

In response to these questions, Environment Ontario funded this project; a three year study designed to determine the sources of PCB contamination in several relatively pristine, inland lakes in central Ontario. The conceptual model for the study was to determine the levels of PCBs in a variety of abiotic and biotic compartments within the lakes in an attempt to determine how sport fish in the upper trophic levels accumulate PCB residues.

Five relatively pristine lakes were chosen for study. In addition, two lakes with known point-sources of PCB contamination were chosen for comparison to the pristine lakes. Throughout 1986 and 1987, samples of water, suspended sediment, bottom sediment, zooplankton, benthos, forage fish and sport fish were collected from each lake for analysis of PCB residues.

The results of this study are summarized in this report. The report is divided into three separate papers, entitled:

a) The relationship between atmospheric deposition and the concentration of 19 PCB congeners in 5 inland lakes in Ontario (Metcalfe and Macdonald).

b) A comparison of PCB congener distributions in two contaminated lakes in Ontario (Macdonald and Metcalfe).

c) Temporal trends and distribution of PCBs in Lake Clear; A small contaminated lake in Ontario (Metcalfe and Macdonald).

The overall project provides some insights into the the role of atmospheric deposition in the contamination of lakes by persistent organic compounds. These data provide an estimate of the baseline PCB contamination of isolated lakes by which future trends in PCB levels can be judged. For instance, if large-scale PCB incineration begins in North America, continued monitoring of isolated lakes may indicate whether inefficient incineration processes are releasing PCBs into the atmosphere. If continued monitoring of isolated lakes indicates no change in PCB levels with

time, this will provide an indication of the persistent atmospheric cycling of PCBs and other organic contaminants; a persistence which may be partially due to volatilization from contaminated regions (e.g. Lake Ontario) and transport to less contaminated regions. In this report, a PCB congener "fingerprint" is identified, which is characteristic of lakes only receiving PCBs by atmospheric deposition. This information can be used by regulatory agencies to identify whether lakes have been exposed historically to point sources of PCB contamination.

Within this report, the PCB data for isolated lakes are continuously compared to data gathered from two lakes contaminated by point sources of PCBs (Rice Lake, Lake Clear). The point source contaminated lakes provide a "positive control" by which the isolated lakes can be evaluated. The PCB data from the point source contaminated lakes also indicate two possible scenarios for the persistence of PCBs in lakes; one scenario in which PCBs disappear rapidly from biota with time (Lake Clear), and another scenario in which the PCB residues in biota remain constant with time (Rice Lake). Either scenario could also occur in isolated lakes receiving atmospheric PCBs, but the outcome may depend upon lake-specific factors (e.g. depth, trophic status).

Finally, this report points out the advantages of an "ecosystems approach" to monitoring of lakes. The monitoring of residue levels in sport fish or sediments alone does not give an accurate picture of contamination within the lake. The complexity of lake ecosystems imposes unique, lake-specific patterns to the distribution of organic contaminants. Factors such as food-chain length, biota lipid content, sediment organic carbon content and lake depth may influence the concentration and pattern of PCBs in any single component of the lake ecosystem, but analysis of the whole system provides a better picture of the contamination problem.